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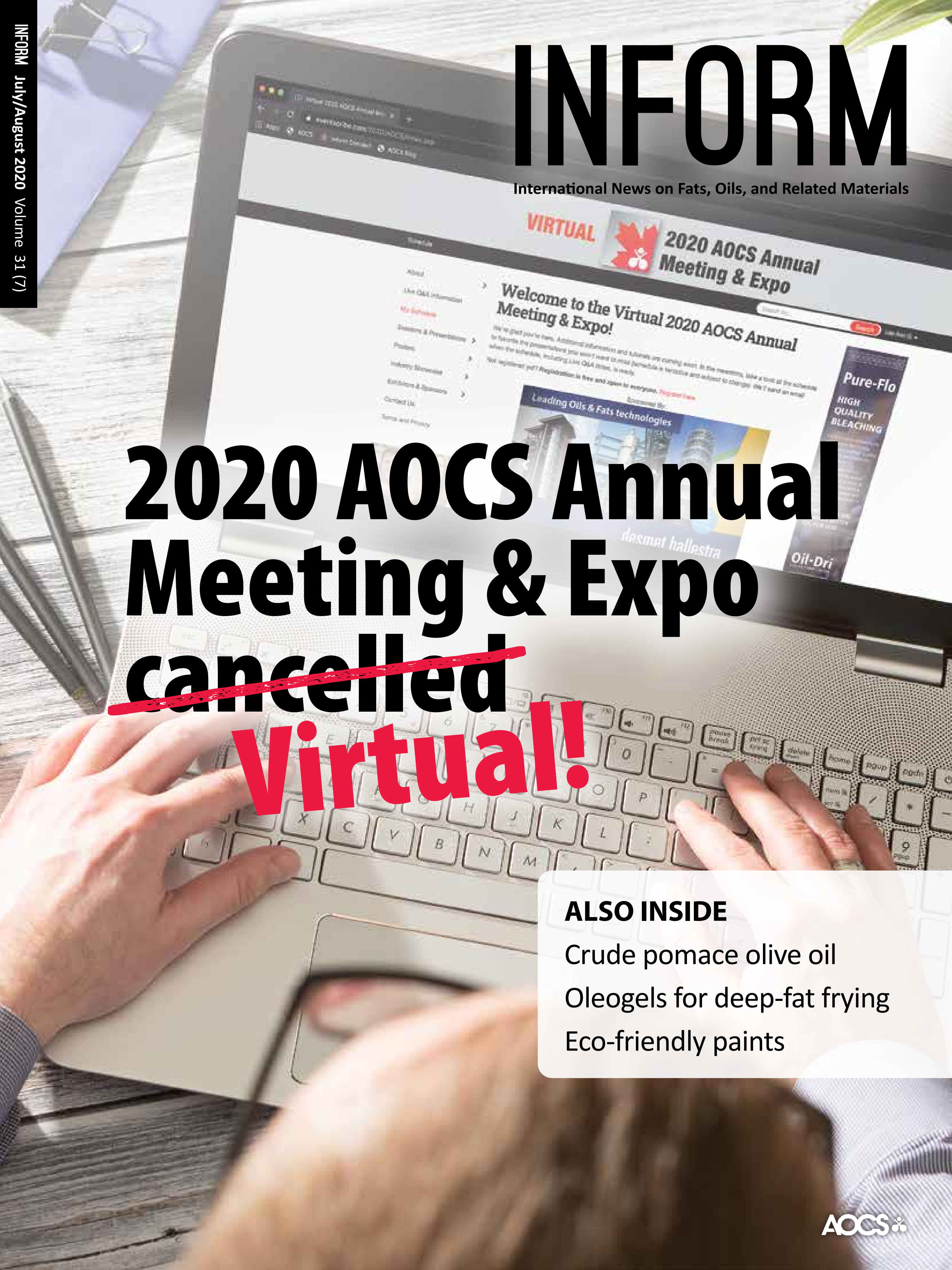
INFORM

International News on Fats, Oils, and Related Materials



2020 AOCS Annual Meeting & Expo ~~cancelled~~ Virtual!

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Eco-friendly paints

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INFORM

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Science highlights from a cancelled 2020 AM&E

Rebecca Guenard

We were all looking forward to the AOCS Annual Meeting & Expo in Montréal, Québec, Canada, April 26–29, but a global pandemic forced us to adjust our plans. In January, reports of respiratory infections caused by a novel virus spreading across Asia, into Europe, and then to the west coast of North America had everyone on edge. As mid-March arrived, it was obvious that slowing the spread of the virus required eliminating its means of transmission. People needed to stay away from each other, and the AOCS governing board made the painful decision that—as much as we relish our time together—the annual meeting would be cancelled.

- **The 2020 AOCS Annual Meeting & Expo would have been held in Montréal, Canada, on April 26–29. However, on March 20th the governing board made the difficult decision to cancel the meeting to avoid the risk of spreading the novel coronavirus.**
- **AOCS received over 500 abstracts for oral and poster presentations on impactful science in the fats, oils, and related industries before the meeting was cancelled.**
- **This article summarizes a few of the interesting technical presentations that would have been given at the meeting. More than 200 technical and poster presentations will be made available during the Virtual 2020 AOCS Annual Meeting & Expo, June 29–July 3, 2020 (annualmeeting.aocs.org), and can be accessed until 2021.**

The AOCS staff shifted gears immediately. From our newly occupied home offices, we considered ways to provide resources to AOCS members and help them experience the meeting as much as possible. We published the @home digest containing research interests, learning opportunities, and career advice. We hosted Executive Steering Committee meetings over Zoom for AOCS' 10 Divisions to transfer leadership between incoming and outgoing chairs and plan for the upcoming year. And, we acquired a digital platform to host the 2020 Annual Meeting online (annualmeeting.aocs.org) to capture the technical content that could not be shared face-to-face (see page 7).

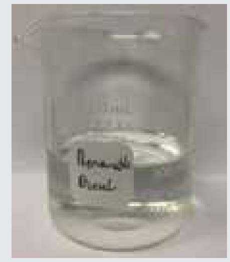
Though our meeting was not in person, it was still an opportunity to share stimulating science. Unfortunately, there are not enough pages in *Inform* for a complete review of everything that was discussed this year. Instead, we offer a brief selection of some of the interesting research that was part of the program.

Displacing petroleum heating oil with biodiesel

Thomas Butcher and Ryan Kerr, National Oilheat Research Alliance, United States, Industrial Oil Products

Last September, the heating oil industry made a resolution to transition to a renewable energy future. The traditionally petroleum-based industry set an ambitious goal to reduce greenhouse gas emissions to 1990 levels. They would start by increasing the amount of biodiesel in heating oil to 20% within the next three years, then to 50% by 2030, with the goal of net zero emissions by 2050.

The NORA (National Oilheat Research Alliance) supports the heating oil industry by conducting research on the technical barriers that may inhibit the achievement of these goals. Biodiesel is an ester, an oxygenated fuel, that will have different chemistry compared to

	 Petroleum No. 2 fuel oil	 Biodiesel	 Renewable diesel (HVO)	 EL[1]
C (w%)	86.8	75.8	85.0	58.3
H (w%)	13.2	12.6	15.0	8.3
O (w%)	0	11.6	0	33.3
HHV[2] (Btu/gal)	138,300	125,300	132,800	95,508
Density (lb/gal)	7.09	7.34	6.51	8.47
Water vapor saturation[3] (F)	120	121	121	121

1. Ethyl levulinate
2. Higher heating value
3. Saturation temperature of flue gas water vapor at 30% excess air

FIG. 1. A list of typical properties for a range of alternative fuels compared to petroleum, including their heating values and saturation temperatures

petroleum, a hydrocarbon. NORA has studied the compatibility of biodiesel fuels with existing oil heating system components, including seal materials, metal piping, and outdoor tanks.

The seals connecting pumps and filters to the rest of a heating oil system are commonly made from a nitrile-based elastomer. NORA has evaluated whether exposure to biodiesel could degrade or somehow compromise such seals. "We do a lot of testing on how different fuels will swell the common elastomers we have in the industry," says Ryan Kerr, NORA lab team member. He immersed the elastomer seals in the fuel and found that in biodiesel it swells to anywhere from six to 20% of its original size. Whereas, with petroleum heating oil, the seals swelled a maximum of 8%. Though the swell value of the elastomer in biodiesel falls below the current allowed standard, some researchers are concerned the fuel could degrade elastomer seals more significantly if it were to break down into organic acids, leading to pump or filter failure. Kerr says that some equipment has started to be manufactured out of the synthetic rubber and fluoropolymer elastomer Viton, instead of nitrile, because it is more compatible with biodiesel. But Thomas Butcher, director of NORA Laboratories, says it is difficult to generalize all nitrile elastomers as problematic in biodiesel applications, since acrylonitrile percentages vary, as do additive and filler amounts. "The story with the elastomers is that people can use, and are commonly using, biodiesel blends with traditional equipment," Butcher explains. "But equipment manufacturers would really like to transition to better elastomers in the future, and that transition has started to occur."

Virtual 2020 AOCS Annual Meeting & Expo

You can learn more by attending the Virtual 2020 AOCS Annual Meeting & Expo, June 29–July 3, 2020 (annualmeeting.aocs.org). The virtual meeting is free to all and includes more than 200 technical and poster presentations, including presentations on three of the topics summarized in this article. Content from the meeting will be available on demand until 2021. Summaries from this article available via the virtual meeting are designated with this symbol of a maple leaf in a speech bubble.

Copper is the primary metal used in fuel systems across the United States, because of its malleability. NORA sought to determine if biodiesel reacts with it. "People are concerned about the stability of biodiesel," says Butcher. "But petroleum hydrocarbons also have stability issues."

The Rancimat test is a common tool to test the degradation of an aging fuel. Kerr exposed samples of biodiesel and petroleum diesel to copper before performing the Rancimat test. The Rancimat induction period decreased rapidly, indicating instability in both fuels after copper exposure. The fuels were also tested for long-term copper storage by incubation above 100°F, which is equivalent to a month of standard temperature fuel storage.

"We saw a lot of polymers forming in the fuels exposed to a copper surface," says Kerr. "There were particulates floating around in these fuels." However, after testing multiple biodiesel fuels, he found that there was less degradation than observed for petroleum. He speculates this is due to the additives incorporated into commercial biodiesel fuels. Kerr says he also tested fuel sitting in a sealed copper line. Without the presence of oxygen, the fuel remained stable. "Overall, we did not find any real-world problems with biodiesel that would require getting rid of all our copper pipe," says Kerr. "Our big caution is if fuel has been exposed to copper, the Rancimat test results will be affected," Butcher adds.

One problem that remains to be addressed is biodiesel's cloud point, which can range from 30 to 55°F for pure biodiesel, depending on the source of vegetable oil. When heating oil tanks are stored outside, biodiesel fuel would not remain liquid during cold winter months when it is needed most. Kerr says they have tested low-voltage tank heaters and tank covers to insulate the fuel from the outside air. The best solution would be to move the storage tank indoors, but that may not be possible depending on the size of the house. Butcher says there may be a chemical solution to this problem. When the biodiesel is composed of unsaturated molecules, cold flow properties improve but the fuel is less stable. Butcher suggests that the industry needs to start considering additives for pure biodiesel that modify its properties to make it a stable liquid at low temperature. Kerr agrees but adds, "We are looking at these non-chemical solutions because right now we have not figured out a molecular one. But maybe in the future that will happen."

Kerr maintains that all the research conducted by NORA shows that biodiesel and petroleum diesel are similar. "There are notable differences, and they will present challenges as we move forward," he says. "But from what we can see now, none of these challenges are unsurpassable." Butcher concludes that the politics and economics of fuels are unknown, but their sole focus at NORA is to ensure there are no technical barriers to using 100% biodiesel as heating oil by 2050.

Research and development for novel pressure sensitive adhesives from vegetable oils

Kaichang Li , Oregon State University, USA, Biotechnology

In 2004, Kaichang Li, chemical engineering professor at Oregon State University in Corvallis, Oregon, commercialized a new wood adhesive made from soybean meal. The protein and carbohydrates from the meal were synthesized into an adhesive for making things like plywood and particleboard. Unlike conventional wood adhesives, the new soybean flour-based products do not contain formaldehyde or other toxic chemicals. Over the past decade, Li has worked with soybean oil in an effort to make a pressure sensitive adhesive for eco-safe tapes and labels, which he hopes will gain as much commercial success as his wood adhesive.

Pressure sensitive adhesives (PSAs) represent a multi-billion-dollar business. The sticky substance is needed for bandages, notes, and stamps, with a significant economic con-

FIG. 2. Kaichang Li inspecting a film coated with a soybean oil-based pressure sensitive adhesive

tribution from the online retail sector. Countless packages shipped around the world everyday require labels and seals, currently produced using petrochemicals.

"I do research on how to develop environmentally friendly products from renewable materials," says Li. "We saw that the existing PSAs were not biodegradable, and we wanted to find a replacement."

His team has discovered how to make novel polyesters from a variety of soybean oil's fatty acids. When oleic acid is epoxidized, for example, the resulting monomer contains a carboxylic acid group and an epoxy group. Polymerizing the epoxidized oleic acid generates a new type of polyester ideal for PSAs. In addition, epoxidized soybean oils can contain multiple epoxy groups, and dimers of fatty acids can contain multiple carboxylic acid groups. The relative content of the epoxy and carboxylic acid groups determines what type of adhesive can be made. For Band-Aids® and Post-it® notes, you do not want the adhesive to be too sticky, says Li. But for other uses, a strong adhesive is necessary.

Li's teams investigated the relationship between the chemical structures of soybean oil derivatives and PSA properties. They characterized molecular structure, thermal stability, and viscoelastic properties, as well as peel strength, shear strength, tack, and aging stability of the PSAs. "We are now able to formulate adhesives for different requirements," he says.

The development of the green adhesives also improves upon current PSA manufacturing practices. Tape and label manufacturers convert a petrochemical-based monomer into a polymer emulsion that is coated onto a film and dried in long tunnels to evaporate the water. Li's adhesive avoids this energy-intensive process that requires expensive equipment. He incorporated the soybean oil polymer into a stable resin that can be shipped directly to a production line. He says, once the resin is coated onto a backing the adhesive can be cured in about one second of exposure to ultra-violet light.

"Our adhesive is less expensive than the petrochemical-based PSAs," says Li, since they do not require a large capital investment for equipment and the excessive energy costs to run them. He is hopeful that the vegetable oil-based adhesives will be commercialized soon.

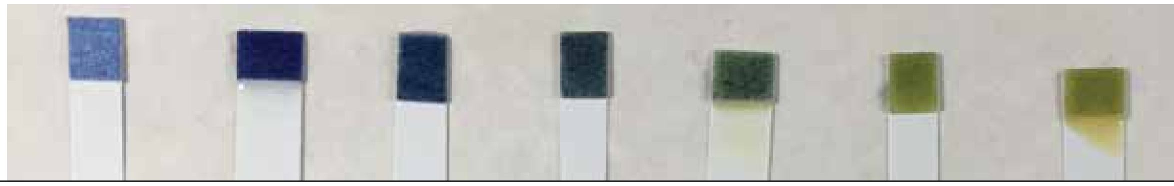
Development of a novel test strip which demonstrates longer fry life of high-oleic oils

Susan Knowlton and John Everard, Corteva Agriscience; Enrique Martinez, Food Quality Testing Corp, USA, Lipid Oxidation and Quality

About five years ago, Susan Knowlton, senior research manager at Corteva Agriscience, was looking for an easier way to measure the end of an oil's fry life, when she met Enrique Martinez, a physical organic chemist interested in food chemistry. Knowlton and Martinez talked about producing a quick, inexpensive test for food industry professionals to determine the quality of their frying oil.

Discrimination between total polar content is apparent within two minutes.

High-oleic soy, 2 min



Total polar content %	**C**	**1.5**	**6.6**	**10.6**	**15.5**	**19.8**	**24.7**

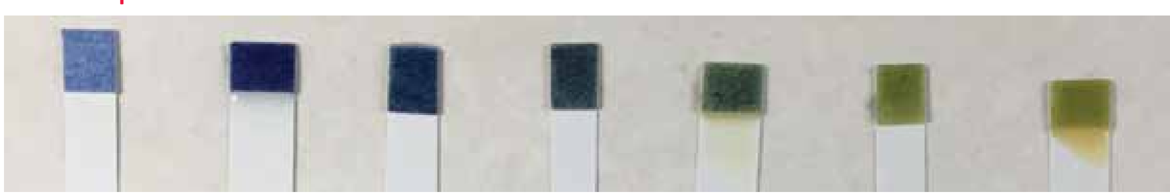
High-oleic canola, 2 min

Total polar content %	**C**	**2.3**	**8.8**	**13.6**	**18.3**	**24.3**

Similar results with commodity oils Oil tested at room temperature

Oil temperature does not change test results.

Room temperature



100°C

Total polar content %	**C**	**1.5**	**6.6**	**10.6**	**15.5**	**19.8**	**24.7**

High-oleic soy, two minutes after exposure

FIG. 3. Test strip results for polar compounds, in a variety of concentrations, for both a high-oleic canola and soybean oil. The dye colors corresponding to increasing polar compound concentration are not affected by the oil temperature, indicating the test strip is robust enough for an industrial kitchen application.

"When you talk to people in the industry, they always say they would love to have a way to objectively determine when it is time to change fry oils," Knowlton, says.

Restaurants want to avoid rancid oil that has polymerized in the fryer, but despite the existence of a few commercially available tests, most prefer arbitrary means to determine if their oil is spent. Whether or not a staff member can see a submerged ladle, for example, or a habitual Sunday oil change regardless of its appearance. Knowlton says there should be a test that serves the needs of the market.

According to regulations in many European Union countries, fry oil must be changed when the concentration of polar compounds—a product of triglyceride decomposition—has reached 25% by volume. Since the EU decided to measure oil quality by polar compound content, Knowlton and Martinez did too. Their team spent several years in the lab developing a test strip that changes color according to the total polar compound concentration in an oil. The strip was tested extensively with controls of purified fatty acids, and mono-, di-, and triglycerides which correlated with a specific color change. They validated their test strip for increasing concentrations of total polar compounds using the AOCS official method as well as modeling with FT-NIR. The prototype and the bench measurements had good correlation, and testing moved to a low-use kitchen. The team set up an experiment in the Corteva cafeteria. Successful measurement there evolved into plans to test the strips in the cafeterias of a large university. Unfortunately, the university closed to prevent the spread of the novel coronavirus, interrupting the study which will resume once the university dining hall reopens. Prior to the outbreak, Food Quality Testing was planning to make the test strips available for purchase this spring.

"Once we get it commercialized, I think it will be very successful," Knowlton, says. "And it will benefit the high-oleic oils space."

With fewer polyunsaturated fatty acids than commodity seed oils, high-oleics represent a more stable product that does not oxidize as easily at high temperatures. They are more expensive than other vegetable oils, but Knowlton says the payback comes in the form of better quality food from an oil with a longer frying life. In the real-world of a functioning restaurant, fry oil life can now be quantified with a test strip, and high-oleic's benefit to kitchen operators will be apparent. "People will see that they get another week out of their high-oleic oil, and it is worth the extra cost," says Knowlton.

Lipid bioaccessibility of cooked meat using the dynamic *in-vitro* gastrointestinal TIM-1 model

Michael Rogers, University of Guelph, Canada, Edible Applications Technology

Associate Professor of Food Science Michael Rogers started his research career curious about how human evolution changed with food preparation. He found a published paper that described physical changes—bigger heads and smaller teeth—that accompanied the onset of cooking over fire in the Northern Hemisphere. The paper provoked him to ask a question: Could he measure a genetic change based on diet? There is evidence of such evolutionary changes present today. Tribes living in the African plains who exist on mostly grains have genes that signal more production of salivary amylase, an enzyme that catalyzes the digestion of dietary starch. Whereas a fishing tribe that eats mostly fish protein has a genetic code that produces less of the enzyme.

Rogers says that today's consumers get more calories from ultra-processed than from whole foods, and he wanted to study if this change in the composition of the foods we eat could be associated with current evolutionary factors, like increased chronic diseases. "Food particles vary in size and elasticity which regulate how fast enzymes can breakdown and absorb the macro and micronutrients of the substrates," says Rogers. He wanted to test how the material properties of food affect the release of their nutrients when the food's composition is identical. In other words, given the same amount of fat, would there be differences in the way a food was digested based on its physical state?

"If a steak is cooked rare, will it digest the same as one that is well-done?" asked Rogers. The steak will have the same amount of protein and calories from fat regardless of how it is cooked, he says. But did the digestion rate depend on the robustness of the food's structural network?

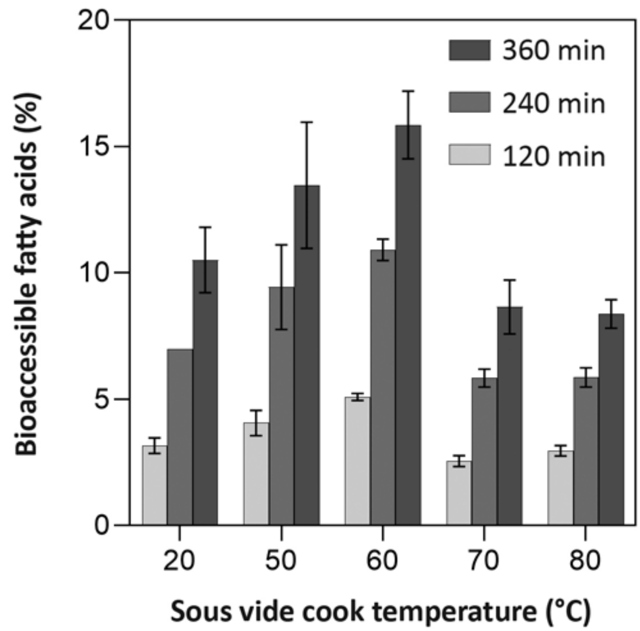


FIG. 4. Results from an experiment on the effect of cooking time and temperature on the bioaccessibilty of fatty acids in a steak measured using a TIM-1 gastrointestinal system

To perform these digestion kinetics studies, Rogers and his student, Elizabeth West, used an *in vitro* model originally designed for pharmaceutical trials, known as the TIM-1 gastrointestinal system. TIM-1 is a dynamic system that simulates peristaltic contractions triggering the release of digestive enzymes and fluids as food transitions through the stomach into the intestines. Roger's team cooked the meat sous-vide style, in a vacuum-sealed bag inside a water bath at low temperature to different degrees of doneness and found that lipid digestion varied with cooking temperature. The lipemic index for a well-done steak is not the same as a rare steak and, though you absorb the fat for both, it takes longer for the fat from a rare steak to enter the blood stream. "The chemistry of a food's lipids is not as significant to the lipemic index as the physical structure of that food," he says. Just like the glycemic index measures blood sugar, the lipemic index indicates the amount of fat in the blood, and rapid increases correlate with detrimental health affects like increased inflammation.

Rogers says he would like to use this data to evaluate whether scientists can design a processed food to have a similar metabolic response to a whole food. Food scientists have devoted many research hours to engineering the stability, palatability, and functionality of foods, he says. "We moved nutritional profile to the backseat. Now it's time to focus on mimicking the biological structures in whole foods to impose digestive barriers in processed foods and slow down the process."

Consumers are becoming convinced that a cell-cultured meat is nutritionally equivalent to animal-derived meat, and that is just not true, says Rogers. "From a digestive perspective, a Beyond Burger behaves more like a confectionary product than a whole food meat," he says. "That is problematic, especially when we are designing a food to replace something that is nutritionally valuable."

Diet has become the determinant of life expectancy, according to Rogers. "We are seeing that people who consume more that 50% of their diet from ultra-processed foods have a higher rate of all-cause mortality across all ages," he says. "Our diet today is actually limiting life expectancy." As climate change continues to affect agriculture, he predicts that the cost of whole foods will increase disproportionally to processed foods. If these lower-cost foods will be consumed by more people, it is important to consider them as a complete system and how that system behaves as a material in the stomach, says Rogers. He hopes to see more food science applied to achieving the same glycemic and lipemic from processed foods that result from eating whole foods.

Real-time process control using spectroscopic techniques

Jonathon Speed, Keit Spectrometers, United Kingdom, Analytical

Originally, the physicists at Keit Spectrometers designed their instruments to analyze the Martian atmosphere. They were lightweight and durable enough to withstand the trip into space. The spectrometer measures molecular vibrations, but—unlike traditional instruments—it was designed to endure vibrations from surrounding equipment without their interference. Unfortunately, the instrument was ready to make the voyage a week *after* the rocket launched. So, Keit turned their attention to potential terrestrial uses.

Product and Applications Manager Jonathon Speed determined that the instrument could function as an online, real-time analyzer for refining processes. This type of technology has been used by the chemical and pharmaceutical industries to streamline manufacturing and reduce costs, says Speed. He believes his analyzer can do the same for edible oil refining.

"Our analyzer can measure the total free fatty acids in the oil, along with a profile of the types of fatty acids that are present," says Speed. He lists fatty acid methyl esters, water, free glycerol, soaps, and hydratable and non-hydratable lipids as a few examples of the compounds the analyzer can measure simultaneously.

According to Speed, the analyzer can be operated in feed-forward and feed-back functions and used to adjust the refining process without stopping production. He says that placing the analyzer at the start of the process to measure crude oil composition means more efficient accounting of refining agents. "You know exactly how much phosphoric acid is needed, because you can measure the concentration of hydratable and non-hydratable lipids," says Speed. "And you also have a value for your free fatty acids to get the caustic dosing exact." However, since no chemical reaction is 100%, he suggests installing the analyzer further along the process to make fine-tuned process adjustments. For example, he says that manufacturers can reduce water use when at the separator stage of the process by analyzing soap content after caustic addition.

Speed acknowledges that reputation of online vibrational spectroscopy measurements was tainted by the unfulfilled promises of NIR analyzers. Those analyzers turned out to be inaccurate, in part, because they required a level of expertise in theoretical chemistry on the part of the operator. Near-infrared analysis requires advanced mathematical models for calibration, since the frequencies it measures are overlapping vibrational overtones that are notoriously difficult to interpret. The Keit spectrometer works in the mid-IR, measuring unique molecular vibrations that undergo pronounced frequency shifts as the oils are processed. This, Speed says, simplifies the analysis. The NIR analyzer became popular first, because, at the time, there was not an FT-IR that could function in a manufacturing environment due to the inherent vibrations associated with the equipment. Speed says the instrument has since been revamped and functions trouble-free in an edible-oil process.

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

AOCS MEETING WATCH

Starting June 29, 2020. Virtual 2020 AOCS Annual Meeting & Expo, https://annualmeeting.aocs.org/.

May 2–5, 2021. AOCS Annual Meeting & Expo, Oregon Convention Center, Portland, Oregon, USA.

May 1–4, 2022. AOCS Annual Meeting & Expo, Hyatt Regency Atlanta, Atlanta, Georgia, USA.

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Valorization of crude olive pomace oil: lipase-catalyzed production of dietetic structured lipids, emulsifiers and biodiesel

Suzana Ferreira-Dias and Natália Osório

- **After olive oil is mechanically extracted from the olives, olive pomace oil is extracted from the pomace with the help of a solvent. Refined olive pomace oil is similar in composition to olive oil and is used for human consumption.**
- **Crude high-acidic olive pomace oils can be directly used to produce value-added compounds, in solvent-free media, by lipase-catalyzed reactions.**
- **Structured lipids, namely low-calorie triacylglycerols, can be obtained by acidolysis of acidic crude olive pomace oil with medium-chain fatty acids or interesterification with medium-chain fatty acid ethyl esters, catalyzed by *sn*-1,3 lipases.**
- **Biodiesel (fatty acid methyl esters, FAME) and *sn*2-monoacylglycerols (emulsifier, *sn*-2 MAG) can be produced by interesterification of crude olive pomace oil with methanol, catalyzed by *sn*-1,3 lipases in solvent-free media.**

Olive oil is the major oil produced and consumed in the Mediterranean countries. During the last 60 years, olive oil production has tripled. The unique flavor properties of virgin olive oil, and its high content of oleic acid (55–83%), polyphenols, and tocopherols with antioxidant properties, can explain the success of the Mediterranean diet. Health benefits of olive oil are recognized by specific health claims for olive oil, such as Commission Regulation (EU) No 432/2012. For the 2019/2020 crop year, the International Olive Council estimates a world production of 3,144,000 metric tons (MT) of olive oil, with the Mediterranean Basin accounting for 93% of that production. The European Union (EU) accounts for about 2,011,000 t, representing 64% of the total world production, with Spain being the major world producer of olive oil (62% of European production), followed by Italy (17% of EU), Greece (15% of EU) and Portugal (6% of EU), according to provisional data at https://www.internationaloliveoil.org/olive-oil-estimates-2019-20-crop-year/.

Olive oil is extracted from the fruit of the olive tree (*Olea europaea* L.) only by physical processes, under extraction conditions, at temperatures (lower than 35°C) that do not promote modifications in the oil. In the last decades, traditional press olive mills have been replaced by continuous extraction mills with centrifugal decanters. The first decanters, called three-phase decanters, could separate three streams: (i) the olive oil, (ii) the aqueous stream (olive mill wastewater containing the vegetation water and some processing water), and (iii) the pomace stream (crushed olive stones and pulp). The olive mill wastewaters are rich in hydrophilic phenolic compounds, which present significant environmental problems when released.

Later, in the 1990s, two-phase decanters were developed to replace the three-phase decanters and overcome the environmental problems associated with the aqueous effluents of press and three-phase decanter extraction mills. In the two-phase decanters, only two phases are obtained: the olive oil and the wet pomace. This wet pomace is a thick sludge, with a 50–70% moisture content, resulting from the blend of the solids and the aqueous phase. The pomace from three-phase systems or from traditional press mills have lower water contents of 40–54% or 22–25%, respectively.

Due to the limited extraction capacity of mechanical extraction methods, the olive pomace still contains 3–4% of residual oil (called olive pomace oil or olive-residue oil), which can be solvent-extracted and used for edible purposes after refining. According to the European legislation, the refined olive residue oil can be sold as "olive-residue oil" after blending it with edible virgin olive oil (Regulation No 136/66/EEC of the Council of September, 22, 1966; Commission Regulation (EEC) No 2568/91of July 11, 1991).

Olive pomace oil has a similar composition to that of the olive oil and can be used as raw material for producing value-added compounds for the food and pharmaceutical/nutraceutical industries, as well as for biodiesel production. Based on our past and on-going research in this area, our research group has proposed an integrated process for the valorization of the crude olive pomace oil. This aim was accomplished by using lipase-catalyzed reactions, following the biorefinery concept and circular economy strategies, to produce: (i) structured lipids (SL); (ii) monacylglycerols (MAG) to be used as emulsifiers; and (iii) biodiesel. Figure 1 depicts the schematic valorization of crude pomace oil developed by our research group.

PRODUCTION OF STRUCTURED LIPIDS

In the last two decades, consumer interest in functional foods has greatly increased, pushing the food industry to produce novel foods with functional properties. Structured lipids (SL) are an example of functional foods with improved technological, functional, and/or pharmaceutical properties. These modified lipids (or fats and oils), which do not exist in nature, are mainly obtained by modification of triacylglycerols (TAG) or phospholipids with respect to their original (i) fatty acid composition or (ii) position of the fatty acids in the acylglycerol backbone, or (iii) synthesized to yield novel TAG (or phospholipids). The reactions can be catalyzed either chemically

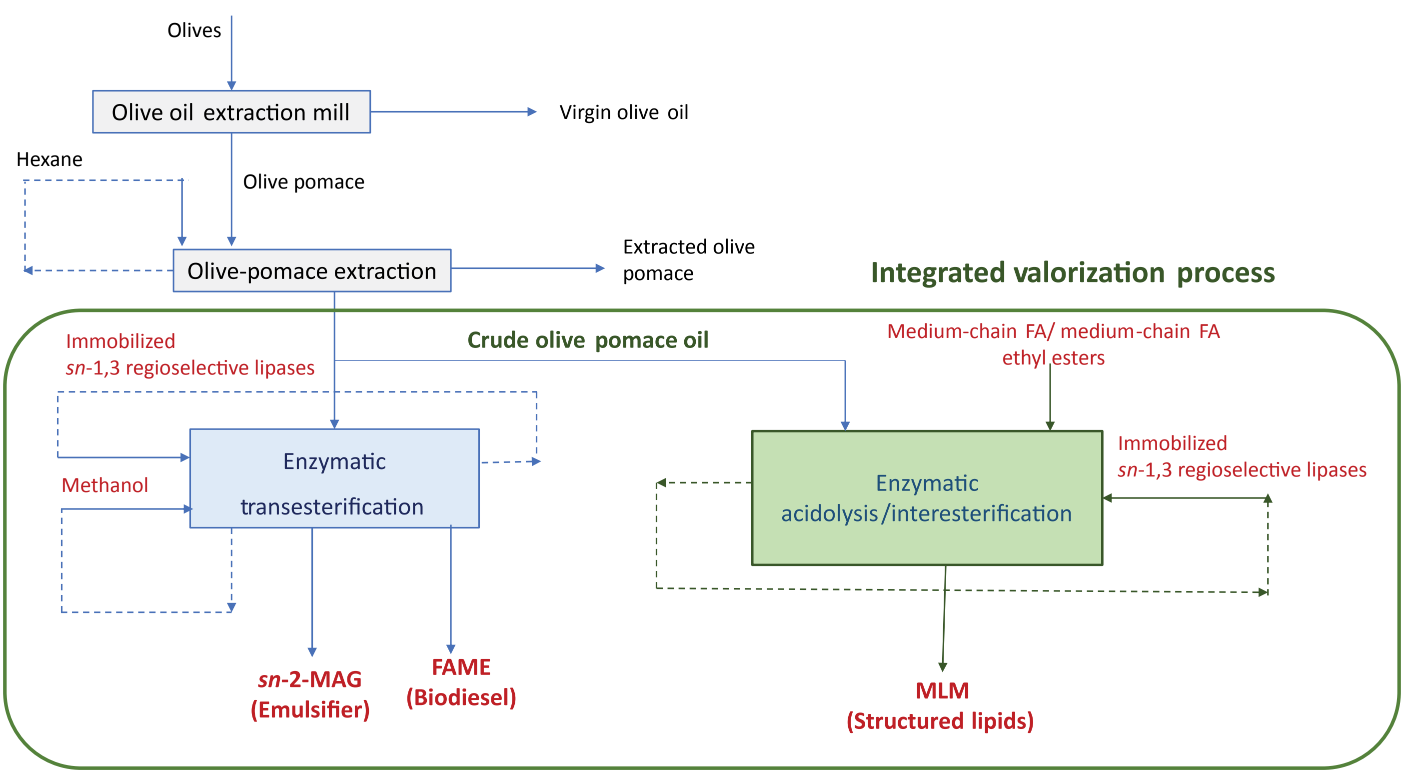


FIG. 1. Schematic integrated process for the valorization of crude olive pomace oil (FA: fatty acids; FAME: fatty acid methyl esters; *sn*-2 MAG: *sn*-2 monoacylglycerols)

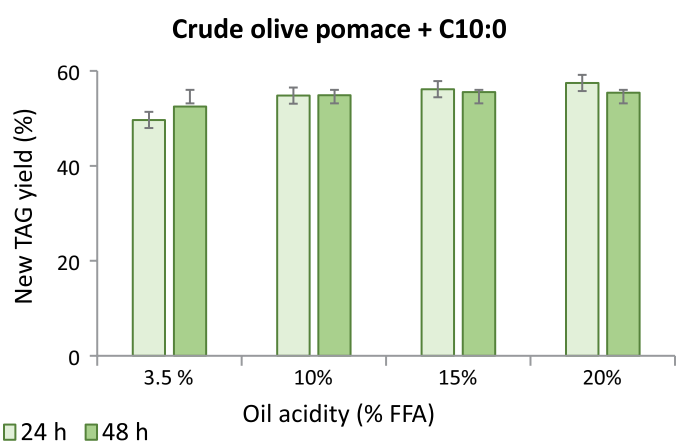
or enzymatically. However, the use of lipases as biocatalysts is highly recommended over the use of chemical catalysts [1, 2].

Lipases (EC 3.1.1.3., triacylglycerol acyl-hydrolase) are enzymes that catalyze the hydrolysis of lipids at oil-water interfaces but, when in non-aqueous media, can catalyze other reactions like esterification and interesterification reactions. Also, conversely to the chemical catalysts, they act under mild temperature and at atmospheric pressure, and present high selectivity toward the substrates (regio-, stereo-, typo-, and substrate selectivity) and reactions. The use of *sn*-1,3 regioselective lipases is especially important for the synthesis of SL since the original position of the fatty acids at the position *sn*-2 is preserved. Fatty acids at the *sn*-2 position are nutritionally beneficial because the absorption of these fatty acids in the form of *sn*-2 MAG is easier than as free fatty acids (FFA). Also, the lack of side-reactions in lipase-catalyzed processes will decrease product recovery and purification costs and, therefore, the number of unit operations. In addition, conversely to the chemical alkali catalysts, lipases can act with acidic crude oils. The use of crude olive pomace oil instead of refined oils will contribute to a reduction in production costs.

Low-calorie dietetic SL is one example of SL that can be produced by lipase-catalyzed reactions from crude olive pomace oil. Low-calorie triacylglycerols are usually TAG presenting a long-chain mono- or polyunsaturated fatty acid (L) at position *sn*-2 and medium-chain saturated fatty acids (M: C6:0-C12:0) at the external positions of TAG molecule. These SL are known as MLM and are important to control obesity, since they present a caloric value of ~5 kcal/g.

Crude olive pomace oil was used to produce MLM by (i) acidolysis with medium-chain fatty acids, namely caprylic (C8:0) or capric (C10:0) acids; or (ii) interesterification with ethyl octanoate (C8 Ethyl), or ethyl decanoate (C10 Ethyl), in solvent-free media, using commercial immobilized *sn*-1,3 regioselective lipases as biocatalysts (*Rhizomucor miehei* lipase, Lipozyme RM IM, and *Thermomyces lanuginosus* lipase, Lipozyme TL IM, kindly donated by Novozymes, Denmark). Crude olive pomace oils with 3.5 to 20% free fatty acids (FFA) and high contents of chlorophyll pigments (91–171.5 mg pheophytin *a*/kg of oil) were used in the acidolysis with caprylic or capric acids, in solvent-free media (Fig. 2). Lipozyme RM IM was shown not to be affected by FFA content of the oils and presented similar performance either in presence of caprylic or capric acid (MLM yields of 53–57%).

Figure 3 shows the time-courses of (i) acidolysis of crude olive pomace oil with 3.5% FFA with C10:0 and (ii) interesterification with C10 Ethyl, catalyzed by Lipozyme RM IM or Lipozyme TL IM. A preference of Lipozyme TL IM for interesterification over acidolysis was observed. Lipozyme RM IM showed similar activity in acidolysis and in interesterification. Apparent equilibrium was attained after 7 h reaction, except for the acidolysis catalyzed by Lipozyme TL IM, which occurred in a much slower rate. Promising results on MLM production from crude olive pomace oil were also obtained with *Rhizopus oryzae* lipase immobilized in ferromagnetic nanoparticles [3].



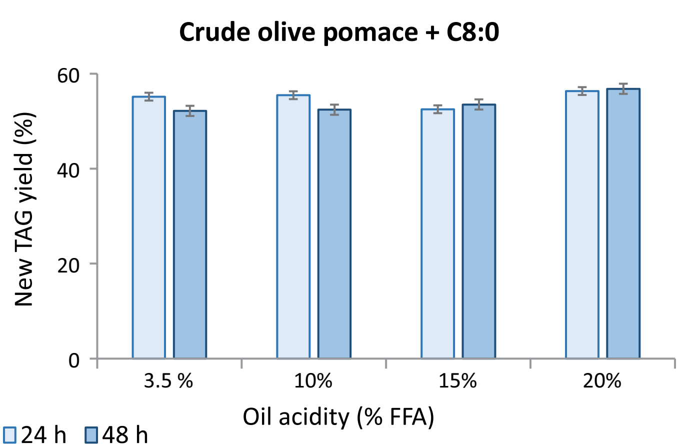


FIG. 2. Production of low-calorie TAG by acidolysis of crude olive pomace with different acidity with caprylic (C8:0) or capric (C10:0) acids, catalyzed by Lipozyme RM IM, in solvent free medium, after 24 or 48 h reaction

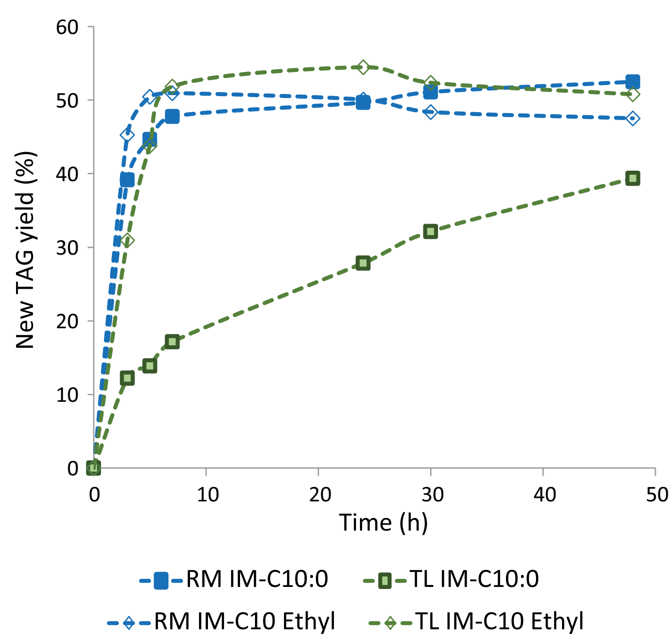


FIG. 3. Time-course of acidolysis of crude olive pomace oil (3.5% FFA) with capric (C10:0) acid, or interesterification with ethyl decanoate (C10 Ethyl), catalyzed by Lipozyme RM IM or Lipozyme TL IM, in solvent-free media

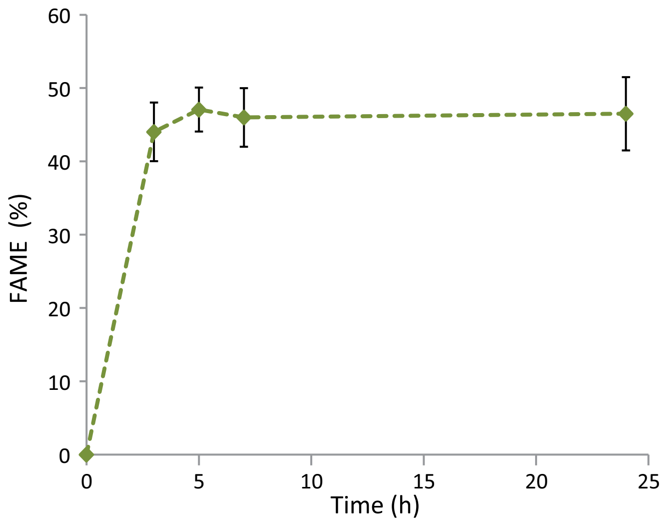


FIG. 4. Interesterification of crude olive pomace oil (20% FFA) with methanol, in solvent free medium, catalyzed by Lipozyme RM IM

PRODUCTION OF BIODIESEL AND MONOACYLGLYCEROLS

Biodiesel consists of blends of mono-alkyl esters of long-chain fatty acids derived from vegetable oils or animal fats, usually fatty acid methyl esters (FAME) or fatty acid ethyl esters (FAEE). Most commonly, refined oils are used, accounting for about 80% of the overall biodiesel production costs [4].

As a novelty of our work, crude olive pomace oil was also used for biodiesel (FAME) production by esterification/transesterification with methanol, catalyzed by immobilized *sn*-1,3 selective lipases, in solvent-free media. Using *sn*-1,3 regioselective lipases, 2 moles of FAME and one mole of *sn*-2 MAG (emulsifier) instead of glycerol, are produced per mole of TAG. The production of monoacylglycerols, which are value-added compounds for the food and pharmaceutical industries, will overcome the problem of surplus of low-quality glycerol produced in biodiesel plants.

The time-course of methanolysis of crude olive pomace oil with 20% FFA, at 50°C and a molar ratio oil/methanol of 1:3, in solvent-free medium, catalyzed by Lipozyme RM IM is shown in Figure 4. Stepwise methanol addition (7 additions) was performed along the first 180 min to avoid lipase inactivation by methanol. The reaction was rather fast, and an apparent equilibrium was attained in about 5 h reaction with a FAME production of 47 mol-%. Since a *sn*-1,3 regioselective lipase was used, the maximum possible to attain was 66.6% FAME. Therefore, the value attained corresponds to about 70% of the maximum theoretical yield. These results show that crude olive pomace oil can be used for biodiesel production, instead of using refined oils, contributing to lower production costs.

Lipases presenting *sn*-1,3 regioselectivity have also been used by several authors, namely by the group of Prof. Diego Luna, from the University of Cordoba, Spain, that patented a biofuel called Ecodiesel®-100. This product consists of a blend of fatty acid ethyl esters (FAEE) and monoacylglycerols in a molar ratio FAEE/MAG of 2:1, obtained by lipase-catalyzed transesterification of refined oils with ethanol [5].

The *sn*-2 MAG obtained in our study can be (i) recovered from the reaction medium and purified; or (ii) remain in the blend with FAME and used as biofuel, similar to Ecodiesel-100.

In conclusion, crude olive pomace oil, instead of refined oil, can be successfully used to produce SL, such as low-calorie TAG, FAME to be used as biodiesel, and *sn*2-MAG that can be used either as emulsifier in food and pharmaceutical industries or in biofuels.

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Medio level macrolipidomics for nutritional research

Klaudia E. Steckel, Juan J. Aristizabal-Henao, and Ken D. Stark

The field of lipidomics emerged from attempts to understand the cellular metabolism of lipids and advances in analytical chemistry that enabled the discovery and measurement of a wide range of lipids. As methods evolved, the "levels" of information about the chemical structure of a lipid molecule that could be determined increased. Standardization of methods and data reporting is necessary for lipidomics approaches to be adopted by the field of nutrition. In particular, lipidomic data must provide fatty acyl species information to allow the data to be compared with existing fatty acid databases.

- **The terms "brutto", "medio", "genio", and "infinio" define the level of information determined about a lipid molecule. Medio level is required for information about the fatty acyls of a complex lipid.**
- **Reports about the lipidome of human plasma have considerable variation and are mainly at the brutto level of information.**
- **Adopting macrolipidomic approaches that focus on characterization of lipid species of high abundance would enable the generation of medio level information necessary for the nutritional scientist.**

MEASURING FATTY ACIDS AND LIPIDS FOR NUTRITIONAL ASSESSMENT

The role of lipids in health and disease are well recognized today, and there is a history of measuring blood "lipids" to assess disease risk. While clinical testing has focused mainly on cholesterol screening and monitoring for assessing heart disease risk, the field of nutrition tends to focus more on assessing the intake of fatty acids. Fatty acid profiling of the food supply is required for food labelling and dietary recommendations for fat that focus on the classes of fatty acids, such as replacing saturated with unsaturated fatty acids.

Blood fatty acid profiling is a useful technique to examine metabolism in nutritional research that is now being used clinically to assess nutritional status. In particular, fatty acid profiles are well-suited for determining the intake of omega-3 polyunsaturated fatty acids, particularly eicosapentaenoic acid (EPA), and docosahexaenoic acid (DHA) typically found in fish. While fatty acid analytical techniques are quantitatively robust, analysis requires that most fatty acids in blood must be removed from their parent molecular lipid, and this information about the molecular lipid is lost. Lipidomic approaches allow for the measurement of these parent or native lipid molecules. Measuring the blood lipidome therefore allows for an assessment of the various fatty acyl species as they exist within complex lipids.

REDEFINING LIPIDOMICS TO FACILITATE STANDARDIZATION

Lipidomic profiling is challenging due to the variation and structural complexity of lipids and wide range in the amounts of each lipid. This has led to a lack of harmonization in the field as many different techniques and methods are used to measure specific types of lipids, but these analyses are still under the blanket term of lipidomics and, thus, seldom have sufficient selectivity for comprehensive accurate quantitation. Before the sample is analyzed, there are variations in sample collection and handling, storage conditions, and sample preparation. The method of introducing the sample into the analytical instrument, the type of instrument, and the settings used to acquire the data can influence the final analytical output. While nuclear magnetic resonance can be used for lipidomics, mass spectrometry has become the most common analytical approach, but there are numerous types and generations of mass spectrometers currently being used for lipidomics. In addition, with the mass spectrometer, samples can be infused directly (shotgun) or after upfront separation by liquid chromatography and/or ion mobility techniques. These variations in the analytical platform and workflow influence the ability to quantify the data but also the quality of the lipid identifications.

Differences in the quality of the lipidomic data are well-documented and have been described as levels of molecular information or hierarchical categories of analytical outputs. These levels refer to the amount of detail known about a molecular lipid starting with information about the lipid class that can be determined with traditional methods such as thin layer chromatography (ie., phosphatidylcholine [PC]) up to completely defined structural lipid molecules with the carbon-carbon double bonds of the fatty acyl isomers defined positionally (D location) and geometrically (E vs Z) which requires advanced techniques in mass spectrometry or nuclear magnetic resonance. While these levels have been identified, the terms that are used to describe them can be inconsistent, so in our laboratory we began using the terms “brutto”, “medio”, “genio”, and “infinio” (the BMGI system) to quickly

communicate the level of information we knew about a lipid molecule that had been identified (Fig. 1).

Basic mass spectrometry analyses provide sum compositional or brutto level information of a lipid that provides the lipid class and the overall number of carbon atoms and double bonds of the attached fatty acyls (ie. PC 38:6). Analysts are fairly confident with lipid identifications at the brutto

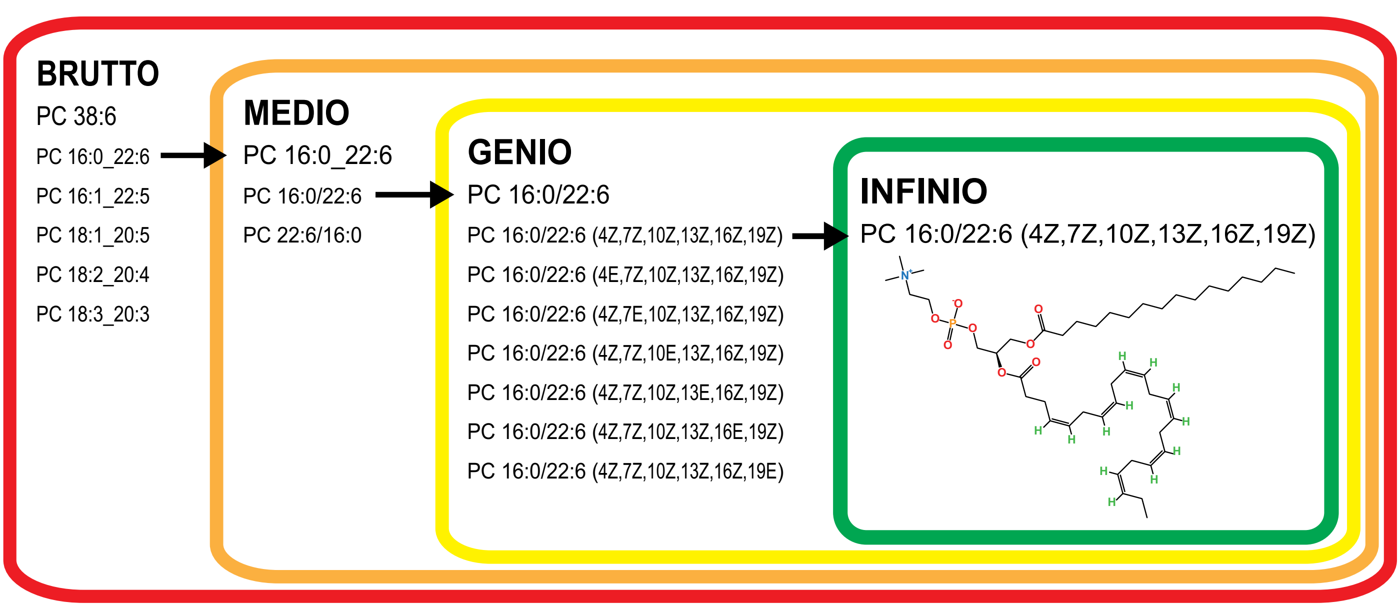

FIG. 1. The BMGI system for identifying the known level of information about an identified lipid using 1-hexadecanoyl-2-(4Z,7Z,10Z,13Z,16Z,19Z-docosahexaenoyl)-sn-glycero-3-phosphocholine as an example.

level, and brutto reporting is common in efforts to standardize lipidomic analyses. Tandem mass spectrometry can identify the fatty acid chains of a lipid and PC 16:0_22:6 could be reported rather than PC 38:6, with the underscore indicating that the location of the fatty acids within the complex lipid is not known. We have described this as the medio level of information about the lipid. When the specific locations of the fatty acids in the lipid structure are determined, a forward slash is used rather than the underscore (PC 16:0/22:6 or PC 22:6/16:0) which we call genio information. We use the term infinio level when lipid structures are fully defined as such, PC 16:0/22:6 (4Z, 7Z, 10Z, 13Z, 16Z, 19Z). While infinio characterization is ideal and should be a long-term goal for the field, it is dependent on high-resolution tandem mass spectrometry with additional separation techniques and/or the generation and detection of chemical adducts and extensive data processing. Medio level lipidomic data could be readily reconciled with existing datasets and knowledge about fatty acids by nutritional scientists.

Obtaining medio level information is possible but it will be an additional burden to ongoing efforts for lipidomic standardization. In 2010, Quehenberger, *et al*., reported on the diverse types and quantitative amounts of the different lipids in a human plasma standard reference material (SRM 1950–Metabolites in Frozen Human Plasma). This comprehensive lipidomic characterization was generated by using 16 different targeted analyses, as untargeted approaches are not capable of capturing this diversity. Despite this effort, only brutto level information was generated for glycerolipids and glycerophospholipids, which are two lipid classes routinely scrutinized in nutritional research. Comprehensive quantitation of the lipidome of a sample is a tremendous analytical burden that limits the adoption of lipidomic approaches outside the core field of researchers and is too costly for routine clinical screening. Focusing on a specific lipid class is a possible solution, but also shifts the analyses away from an omics-approach. Alternatively, we have proposed that lipidomic analyses be categorized as "macrolipidomic", representing efforts to characterize high abundant lipids in a sample, versus "microlipidomic", where low abundant lipids are measured.

THE HUMAN PLASMA LIPIDOME

Human plasma is used commonly in biomedical research and clinical assessment. As plasma is aqueous, the bulk of plasma lipids are found as part of lipoprotein complexes with smaller contributions from lipids interacting with plasma carrier proteins such as albumin. In general, glycerophospholipids, triacyglycerols, cholesterol, and cholesteryl esters comprise approximately 90% of the plasma lipids of a healthy adult after an overnight fast, with unesterified fatty acids and their metabolites, and sphingolipids making up most of the remaining 10%. As mentioned above, SRM 1950 is a human plasma reference material available through the National Institute of Standards that has been used in attempts to characterize the plasma lipidome (Table 1). SRM 1950 has established certified, reference, and information values of various metabolites, including cholesterol, total glycerides, and 27 fatty acids that are routinely measured in lipidomics.

Quehenberger, *et al*., 2010, on behalf of the LIPID MAPS consortium (www.lipidmaps.org), originally identified 588 species in the plasma lipidome. Their concentrations resembled the validated levels of lipids in SRM 1950. More recently, Bowden, *et al*., 2017, used SRM 1950 in an interlaboratory exercise for lipidomic measurements. The 31 laboratories involved identified 1,527 species. Consensus values for lipids consistently reported by ≥5 labs were generated using a median of means method, resulting in quantitative estimates for 339 species. The sterol lipids amounts were higher and glycerolipid and glycerophospholipid amounts were lower than the previous Quehenberger report. These studies also revealed considerable heterogeneity in lipidomic approaches. The original LIPID MAPS report identified a high number of sphingolipids and "eicosanoids" within the fatty acyl class as compared with the consensus values of the interlaboratory exercise, and

TABLE 1. Lipids in Standard Reference Material 1950–Metabolites in frozen human plasma

Lipid category	Defining the plasma lipidome 2010[a]		Interlaboratory Harmonizing Exercise 2017[b]		
			All labs	Consensus (≥ 5 labs)	
	Species (number)	Sum (mg/dL)	Species (number)	Species (number)	MEDM[c] (mg/dL)
Fatty acyls	107	6	177	14	7
Glycerolipids	73	94	317	83	54
Glycerophospholipids	160	201	679	150	108
Sphingolipids	204	24	236	58	26
Sterol lipids	36	146	118	34	230
Prenol lipids	8	0.4	-	-	-
Total	588	471	1527	339	424

[a] Quehenberger, O., *et al., J. Lipid Res. 51*: 3299–3305, 2010.
[b] Bowden, J.A., *et al., J. Lipid Res. 58*: 2275–2288, 2017.
[c] MEDM (median of means method) used to generate a consensus value from laboratory values.

both studies reported relatively low numbers of glycerolipids despite the high quantity of this latter class of lipids.

NUTRITIONAL LIPIDOMICS

The glycerolipid and glycerophospholipid lipid classes have significant roles in nutrition. Over 90% of the dietary fat consumed is in the form of glycerolipids, and plasma glycerolipids vary dramatically across individuals, with diet having a major influence. The fatty acid compositions of glycerophospholipids are used to identify biomarkers of diet and disease risk with plasma and erythrocytes, and to link cell membrane structure to biological function in tissues, such as heart, brain, and liver. Lipidomic profiling efforts have tended to report only brutto level glycerolipid and glycerophospholipid identifications. We believe that medio level characterization of the macrolipidome can be developed into a feasible analytical approach for nutritional applications. Lipidomics could then be used for transformative insights into dietary biomarkers, the metabolic impact of diet on health and disease, and the individual lipids within the food supply.

Klaudia Steckel is a MSc student in the Lab of Nutritional Lipidomics at the University of Waterloo, Ontario, Canada. Her research focuses on determining the macrolipidome of human plasma with different mass spectrometry platforms and acquisition modes.

Juan Aristizabal-Henao developed macrolipidomic and microlipidomic methods during his PhD at the University of Waterloo. Currently, he is a postdoctoral fellow at the University of Florida, where he continues to develop novel mass spectrometry methods to examine the relationship between lipids, metabolites, and contaminant exposure in health and disease.

Ken Stark is a Canada Research Chair in Nutritional Lipidomics and Professor in the Department of Kinesiology at the University of Waterloo. He has expertise in fatty acid and lipid analytical methodology and the role of diet on lipid blood biomarkers.

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Oleogels as alternatives for frying fats and oils

Bertrand Matthäus, Madline Schubert, Nelli Erlenbusch, Inga Smit, Lydia Weber, and Sharline Nikolay

Deep-fat frying is one of the most popular applications for the preparation of food. It is fast, simple to handle, and results in highly accepted products due to the typical smell, taste, and palatability of fried food. One pivotal aspect in the production of high-quality fried food is the selection of an appropriate frying medium. During the frying process, oil or fat serves as a medium that transfers heat from the heating source to the food [1]. Another important task of the frying medium is to enhance food's flavor, which is responsible for the typical smell and taste of fried products. The selection of a suitable frying medium is also crucial for the quality of the final product. This is because a lot of fat or oil is taken up by the food, and the high amounts of fat in fried food influence its shelf life, aroma, texture, and surface properties.

- **Oleogels are structured vegetable oils that behave like solid fats but have the same nutritional properties of liquid vegetable oils.**
- **Our research group recently did the first promising experiments to evaluate the use of oleogels in deep-fat frying.**
- **This article describes the first initial results.**

Over the last 50 years, the trends for using fats and oils in food processing have changed several times, driven especially by consumer awareness about nutritional quality. Fifty years ago, animal fats were very popular due to their technological properties and high storage stability. Later, animal fats were replaced by partially hydrogenated oils (PHO) due to concerns about the high cholesterol contents of animal fats. Then, PHO was banned in many countries because they contain trans-fatty acids, which are suspected to cause cardiovascular heart diseases [2].

Palm oil or modified fats became the replacement, but this has prompted strong discussion about environmental impacts and the high content of saturated fatty acids. Today, the use of highly stable liquid high-oleic oils or blends of different vegetable oils are preferred as a frying medium. They display some advantages with respect to nutritional aspects due to low amounts of saturated fatty acids, high contents of monounsaturated fatty acids, and an oxidative stability that is comparable with solid fats. On the other side, the application of liquid oils gives fried food a greasy surface and causes oil leakage during long-term storage.

WHAT ARE OLEOGELS?

Thus, the search for alternative fats or oils for food processing is an ongoing story. One promising alternative to conventional frying media are oleogels. Oleogels have technological properties that are similar to those of solid triacylglycerol structured fats, but they display the nutritional properties of liquid vegetable oils. While the structure of solid fats results

from saturated fatty acids, which have a more-or-less linear structure and therefore allow a compact assembly of fatty acids, oleogels mainly consist of liquid oil and a small amount of a structuring agent known as an organogelator.

Therefore, oleogels contain a high amount of unsaturated triacylglycerols, but the solid structure is provided by the organogelator, which forms a 3-dimensional network in which the liquid oil is incorporated. Since the unsaturated fatty acids in the oleogel are not changed, the nutritional value of the liquid oil is preserved [3]. Many different structuring agents are applicable, such as ethyl cellulose, monoacylglycerols, fatty acids, phytosterols, alcohols, or waxes. Ethyl cellulose and monoacylglycerols, for example, are already approved as food additives, waxes, such as sunflower wax (SFW), have not been approved yet. The preparation of oleogels is a simple process that includes heating and stirring of the liquid oil in combination with the organogelator, just above its melting point. Finally, the mixture is cooled down to allow the formation of a gel-like structure, in which the liquid phase is embedded [4].

OLEOGELS AS PROMISING ALTERNATIVES FOR CONVENTIONAL FRYING MEDIA

The application of oleogels for food processing has been presented in the literature for some products [5–7], especially for bakery goods [8–10]. Only one scientific study has been published on the application of oleogels as an alternative to high saturated-fat frying media [11]. In this work, soybean oil-based oleogels with carnauba wax as organogelator, were used to prepare instant fried noodles. The resulting products had a similar texture and more favorable fatty acid composition than noodles fried in saturated fat.

An alternative to carnauba wax obtained from leaves of the palm *Copernicia prunifera,* SFW is a natural constituent of sunflower seeds. This wax forms a protective layer on the seed surface, and noticeable levels are extracted with the oil during oil processing. These high-melting waxes solidify at room temperature, causing a visible white precipitation that is unappealing to consumers. Therefore, waxes are removed from the oil during oil processing by winterization, leading to a large quantity of SFW that is readily available. SFW has not been approved as food additive yet, but since its molecular structure is similar to that of carnauba wax, SFW is likely to pass through the digestive tract unaltered as well—and to be approved in the coming years.

Compared to frying with conventional fats, the application of rapeseed oil-based oleogels with SFW as an organogelator for the preparation of potato crisps or French fries offers several advantages: optimized surface properties, improved multi-sensory perception, and a more healthful fatty acid profile that is lower in saturated fat and higher in unsaturated fatty acids but has comparable technological proper-

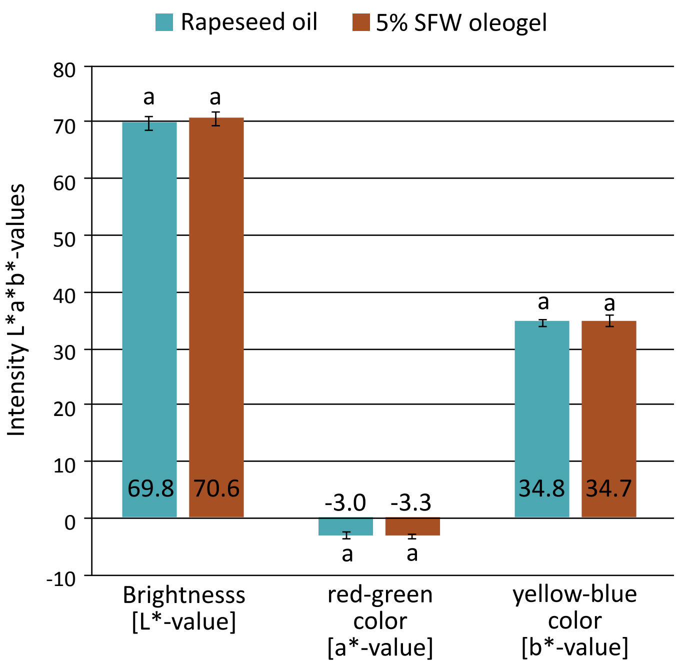

FIG. 1. Color of French fries fried in rapeseed oil and 5% SFW oleogel in the CIELAB color room

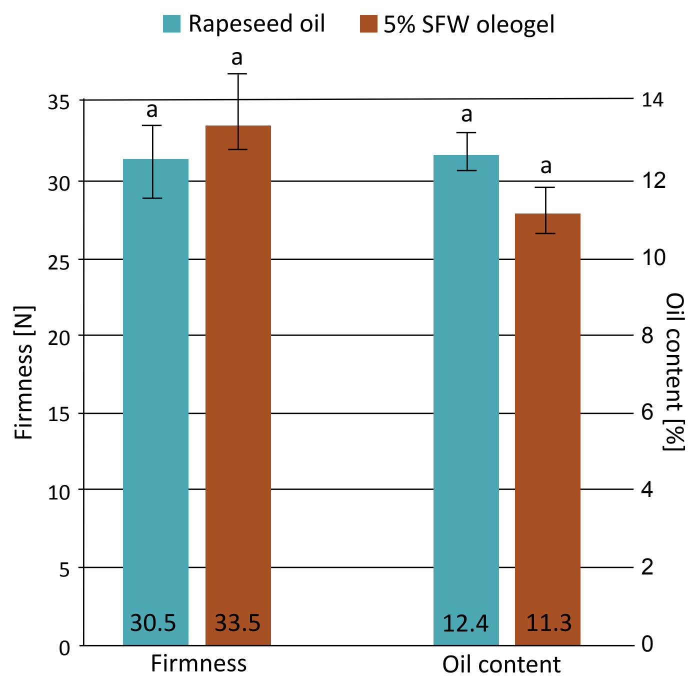

FIG. 2. Comparison of the firmness and oil content of French fries fried in rapeseed oil with those fried in 5% SFW oleogel

ties. Another important aspect in this context is that oleogels become solid again after deep-frying, when the fried food cools down. This should result in a significantly less oily surface and, possibly, a lower fat uptake. In a first experiment, these aspects were proven by using a SFW-based oleogel as a frying medium for commercially available par-fried French fries.

SUNFLOWER WAX-BASED OLEOGELS (5% SFW) IN THE FRYING PROCESS

Parameters for the evaluation of ready-to-eat French fries are texture, color, and oil content. In addition to sensory quality, these parameters determine the acceptance of products by consumers. Thus, when using an oleogel-based frying medium, it is paramount that these parameters are comparable with that of conventional frying media. Furthermore, the application of the organogelator should not impair frying performance of the frying medium.

Chemical results

No significant differences in the chemical parameters used to assess frying oil quality (such as polymer triacylglyerols or total polar compounds) were observed after 20 frying cycles with rapeseed oil-based oleogels versus rapeseed oil. Therefore, it can be concluded that the use of SFW does not significantly influence the frying performance of rapeseed oil.

Color

The color of fried French fries gives some indication of reactions in the context of the non-enzymatic browning (Maillard reaction), which takes place in the crust at higher temperatures when the moisture content of the product decreases in the presence of reducing sugars and asparagine as amino acid. When measuring the color of fried French fries, the amount of reflected light on the surface of the food is recorded, and the results are given in a color space. A common standard for a color space is the L*a*b* color space established by the International Commission for Eclairage (CIE) in 1976. The three parameters of this model represent the brightness of the color (L*), its position between red and green (a*), and its position between yellow and blue (b*) [13]. The CIE-L*a*b* color system is based on the spectral range of the sensitivity of human vision. A comparison between French fries fried in rapeseed oil or in 5% SFW oleogel showed no significant difference between the three parameters of the CIELAB color room, so an influence of the frying medium on the color development can be excluded (Fig. 1). It can be assumed that the quality of the raw material and processing conditions have a stronger influence on the formation of Maillard reaction products and, therefore, on the color.

Firmness

The firmness of French fries strongly influences consumer acceptance. It is determined by chemical and physical changes that take place during the frying process in the product, e.g., release of intracellular materials, starch gelatinization, dehydration, crust formation, breakdown of adhesive forces between cells, water evaporation, and tissue expansion [12]. Firmness of French fries was measured by a texture analyzer and gives some impression of the crispness or hardness of the French fries with special consideration to the crust. Ten French fry sticks of nearly the same size were placed close together on the base platform of the texture analyzer, and the force needed to press a knife 5 mm deep into the sticks was measured. The results showed that the French fries fried with rapeseed oil were a little less firm than the French fries prepared with 5% SFW-based rapeseed oil oleogel. However, the difference was not significant (Fig. 2).

Fat content and fatty acid composition

Depending on the frying temperature, type of fryer, and quality of the raw material, fried French fries contain between 12 and 18% fat. From a nutritional point of view, a lower fat content is recommended to reduce fat intake. Frying with a 5% SFW oleogel resulted in 1% less fat intake (11.3%) compared to 12.4% fat intake for frying with rapeseed oil (Fig. 2). However, the difference between the two frying media was not significant.

Today, the fatty acid composition of food influences consumer purchasing decisions. The optimal fatty acid composition should have low levels of saturated fatty acids, a high level of monounsaturated oleic acid, and a ratio of linoleic to linolenic acid of 2:1. The proportion of trans-fatty acids should not exceed 2 grams per 100 g of fat [14]. Figure 3 shows the fatty acid compositions of rapeseed oil and 5% SFW oleogel compared to conventional frying media. There was no significant difference in fatty acid composition between rapeseed oil and 5% SFW oleogel. The content of trans-fatty acids was low for the different oils except for partially hydrogenated oil, which had more than 10% trans-fatty acids. In the other oils, trans-fatty acids are formed to a low-level during refining, which today should be below 1%. Palm oil is characterized by a high content of palmitic acid, while rapeseed oil shows the highest content of polyunsaturated fatty acids.

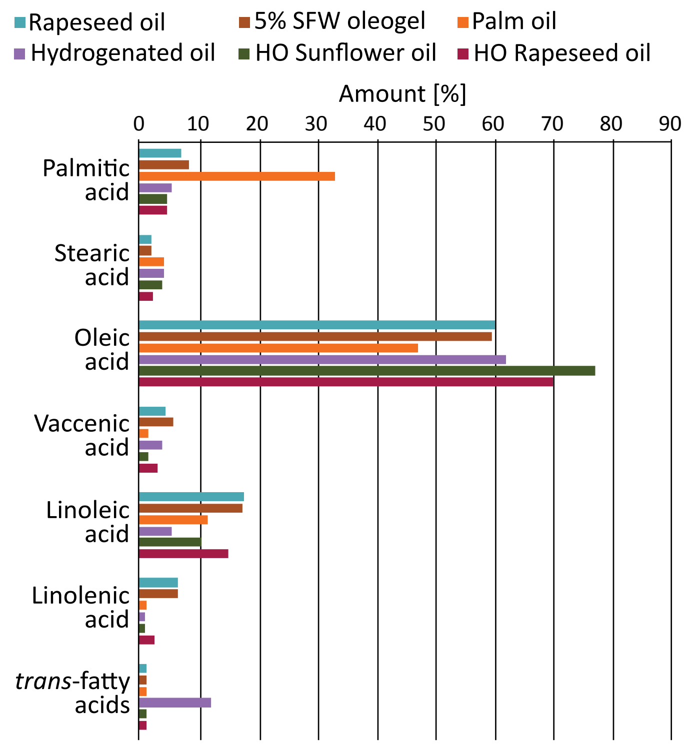

Fig. 3. Fatty acid composition of different conventional frying media and 5% SFW oleogel

Sensory evaluation

Another important factor that influences consumer purchasing decisions is the sensory quality of food. Products that do not meet consumer expectations will not have a chance on the market. A common method of comparing products is the pairwise comparison test with consumers known as DIN EN ISO 5495:2007. In this test method, the examiner is given two samples and asked to identify the sample with the most pronounced characteristic.

The results of the sensory evaluation (Fig. 4, page 26) show that the surface of French fries was assessed by testing the French fry sticks between the thumb and index finger. Those sticks fried in 5% SFW oleogel were determined to be

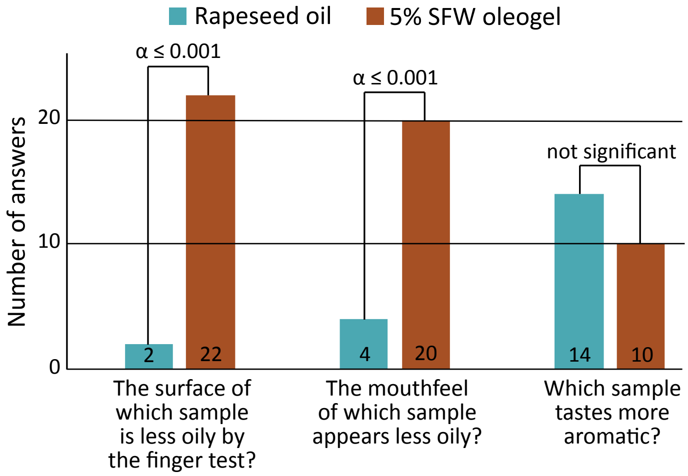

FIG. 4. Sensory evaluation of French fries fried in rapeseed oil and 5% SFW oleogel

less oily. The mouthfeel of French fries fried in 5% SFW oleogel was also characterized as less oily, demonstrating that the use of oleogel as frying medium resulted in the perception that the fried product was less oily. Finally, there was no significant difference in the taste of French fries fried in different types of frying media, indicating that the use of SFW-based oleogels did not impair the taste of the final product.

These initial results of our frying experiment indicate that oleogels based on rapeseed oil with SFW as an organogelator are a promising alternative for solid fats rich in saturated fatty acids. The final products were comparable with respect to texture and color but had a slightly lower fat content, which is desirable from a nutritional point of view. Most important is that products fried in 5% SFW rapeseed oil-based oleogels were perceived to be less oily than French fries fried in liquid oil. This means that the solid structure of the oleogel improved the quality of the French fries. However, for the industrial application of SFW-based oleogels in food to move forward, it is essential to advance the approval of SWF. In addition, further work is necessary to evaluate different types and amounts of organogelators to optimize the frying process.

Bertrand Matthäus, Madline Schubert, Nelli Erlenbusch, Inga Smit, Lydia Weber, and Sharline Nikolay are all working at the Max Rubner-Institut, Department of Safety and Quality of Cereals, in Detmold, Germany. Bertrand Matthäus can be contacted at bertrand.matthaus@mri.bund.de.

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Can a truly eco-friendly paint satisfy consumers?

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

Rebecca Guenard

Redecorating or moving into a new home means exposure to myriad volatile organic compounds (VOCs) that escape from architectural coatings. Many of today's consumers are trying to minimize such exposure, especially if they have young children or suffer from asthma or allergies. Formulating to match consumer expectations for durability and cleanability while also eliminating VOCs remains a seemingly insurmountable technical challenge despite decades of research. Greener ingredients have been the industry's primary achievement, but is it possible to make paints and coatings truly eco-friendly?

In 2017, the Federal Trade Commission (FTC), a United States government agency responsible for consumer advocacy, charged four paint companies for deceptively promoting their products as emission-free or containing zero VOCs (https://www.ftc.gov). The companies made explicit claims that their paints were safe for babies, children, and pregnant women. The FTC alleged they had no evidence to support the claims. Two of the paint companies went as far as creating seals to mimic validation of their safety claims by a third.

"All paints release chemicals when being applied and while drying," the FTC statement reads. "Some of these chemicals can be unsafe—especially to babies and people with asthma or allergies."

The FTC ordered that the companies demonstrate their paints contain zero VOCs and emit zero chemicals over their lifetime or that they satisfy trace-level emissions tests from the point of application and beyond. The following year a settlement was reached. In lieu of emission testing that demonstrated trace emissions at all times, the agreement specified that a manufacturer may substantiate zero VOC claims by demonstrating that the paint has trace levels of emission six hours or less after application. The case exemplifies the complexity associated with producing an all-natural paint.

The chemical composition of paints vary depending on color, durability, and other properties. In general, pigment particles suspended in a binder are dissolved in a solvent. The volatile components evaporate from the drying film after application, while the binder holds the pigment in the dry film, causing it to adhere to the substrate. The main organic solvents used in paints are toluene, xylene, aliphatic compounds, ketones, alcohols, esters, and glycol ethers. Nowadays, solvent-based paints contain much less solvent—and less hazardous solvents—than a decade ago, often similar to water-based paints. In addition to these primary components, paints contain additives which may improve its finish and durability, or prohibit bacteria growth.

Illness caused by the release of VOC's from construction materials have led public health officials to coin the phrase, "sick building syndrome". The green building movement, ironically, exacerbates the problem. Houses are sealed tighter for improved energy efficiency, which impedes the escape of VOCs. The German government has established guides for total VOC exposure that could pose health problems based on current toxicological and epidemiological knowledge (https://www.umweltbundesamt.de). For short term exposure, such as during home improvement, their total VOC recommendation is 10–25 mg/m^3. "In rooms intended for longer-term residence, the TVOC value in the range of 1–3 mg/m^3 should not be exceeded," read the guidelines. "Ideally, TVOC concentration in indoor rooms should reach a maximum long-term average of 0.2–0.3 mg/m^3 or lower if possible." Similar guidelines in Japan provoked one research group to measure VOC values from paints and sealers (https://doi.org/10.1007/s13762-018-2093-0). The researchers found that some of the products in their study exceeded recommended limits (Fig. 1).

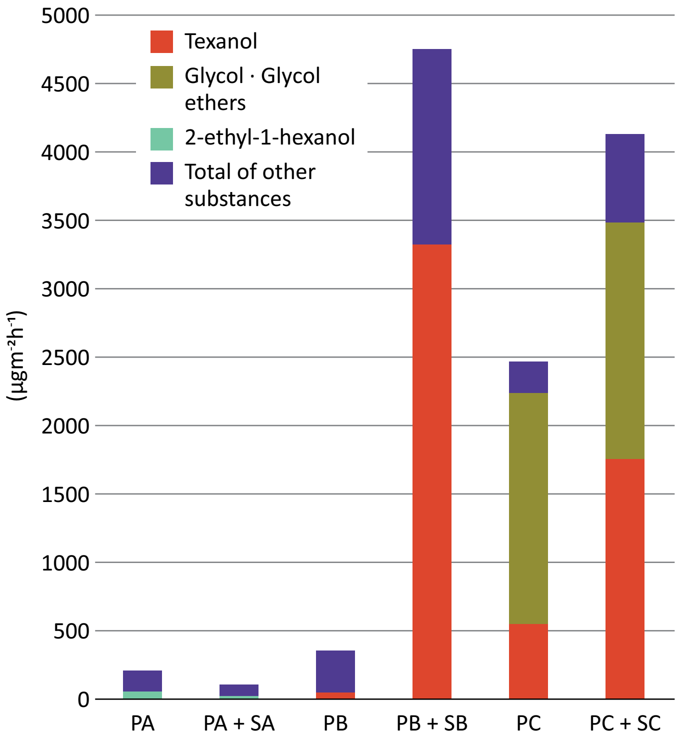

FIG. 1. Emission rates of three different paints (PA, PB, and PC) and three sealers (SA, SB, and SC) combined with paint from the same manufacturer. Source: Suzuki, N., Nakaoka, H., Hanazato, M. *et al.*, *Int. J. Environ. Sci. Technol. 16*: 4543–4550, 2019.

Humans have been making paint since society began. There is evidence to suggest that nearly 50,000 years ago, during the stone age—a time before humans raised domesticated cattle—people manufactured paint using ochre and casein from bovid milk. Researchers can only speculate about how the paint was used, possibly to adorn the body for rituals or maybe to decorate surfaces. Regardless, early humans mixed milk with a dye to create paint. Later, they would realize that heating the milk in limestone precipitated solid chucks of casein that acted as a binder to better adhere the paint to surfaces. Thus, paint formulation began, and humans have tinkered with it ever since.

Linseed oil, also called flax seed oil, was mixed with resins to varnish mummy cases in the time of the Egyptians, a formulation that endured for centuries spurred by such enhancements as incorporating the volatile organic solvent turpentine to improve viscosity. Alongside these oil-based formulations, milk paints also remained popular, each serving specific purposes. Oil-based paint dries to a smooth sheen, best for wood surfaces, while milk paints work well on porous, plaster surfaces and were popular throughout the colonial era. Synthetic compounds produced by the petrochemical industry eventually replaced natural ingredients and gave paint manufacturers more control over their finish properties. Through the decades, they grew in popularity until environmental regulations and consumer pressure caused formulators to consider how they could retain the desired durability and cleanability of a paint while making it more eco-friendly.

In the early 2000s, raw material suppliers like Archer Daniels Midland and DuPont helped paint companies increase sustainability and decrease VOCs by creating bio-based replacements for petrochemical ingredients. Some consumers feel continued improvements are needed, aiming for paints and coatings with zero VOCs and all-natural ingredients. Asian Paints, an Indian company, recently promoted a line of paints using soybean, whey protein, casein castor seeds, calcium carbonate, neem oil, and pigments (https://www.thehindu.com). The company is following the lead of brands like The Real Milk Paint Co., which has resurrected the milk protein paint formulations of old to offer customers an eco-friendly product. According to an Asian Paints spokesperson, their product is odor-free because it has no VOCs, but customers will have to accept a different wall-coating experience. The company describes the paint's flat finish as having a vintage feel and indicates that homeowners will need to touch-up their walls regularly, because the paint cannot be washed. "Since there are no chemicals, the paint is not washable. Ensure you only use a dry cloth to clean the surface," said the spokesperson.

For now, all-natural paints remain a niche market. Until paint manufacturers develop new technology to enhance the ruggedness of natural paints, most consumers seem satisfied with the low-VOC products formulated two decades ago. Biotechnology researchers are investigating the compounds bacteria rely on for survival in an effort to usurp their synthesis process for paint formulations. Primary candidates include marine bacteria that naturally produce water-proofing or corrosion-resistant (https://doi.org/10.3390/app9122409) compounds, along with bacteria that enzymatically create dyes (https://www.pnas.org/content/115/11/2652). Researchers are hopeful they can manipulate these bacteria and mass-produce compounds with improved sustainability and toxicity over those that are currently petrochemically-derived. Such experiments have been successful for other applications, perhaps someday these bacteria will unveil the secret to applying a sturdy surface coating without releasing VOCs.

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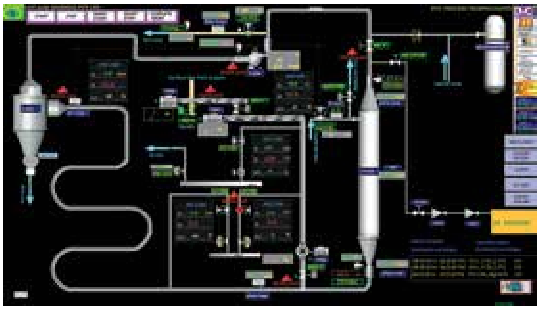

China publishes final text of regulation governing new chemicals

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

China's Ministry of Ecology and Environment (MEE) published the final legal text of the country's revised overarching regulation governing new chemical substances on May 7, 2020.

The new MEE Order 12 replaces the current MEP Order 7 and will come into force on January, 1, 2021, when the existing Order will be repealed.

The government approved the revisions to the regulation (unofficial English title, New Chemical Substance Environmental Management Registration Measures) February 17.

The revised regulation:

- strengthens the management of persistent (P), bioaccumulative (B), and toxic (T) new chemical substances;
- sets out the conditions when the government will not approve new chemical substances that meet PBT criteria;
- reduces requirements for some polymers of low concern and registration of new substances manufactured or imported in volumes of less than 10 metric tons (MT) a year; and
- introduces a notification process for new uses of existing listed substances, similar to the significant new use rule (Snur) under the US Toxic Substances Control Act (TSCA).

If a new substance meets all three criteria—P, B, and T—the MEE will not approve it. If it meets two—PB, BT, or PT—the substance can be approved but with conditions such as annual reporting and inclusion in the Inventory of Existing Chemical Substances (IECSC) with use restrictions.

Under the current MEP Order 7, there are no criteria outlining how the government will refuse approval for new substances.

SCOPE

The regulation requires the following to be notified:

- new substances (substances not listed on the existing inventory); and
- new uses (this covers existing substances that are listed on the inventory but are subject to new use management).

Under Order 12, when the MEE adds a highly hazardous new substance to the inventory, it will specify its permitted uses.

Any company wishing to manufacture, use, or import the substance for a different (non-specified) use will need to submit a new chemical substance notification for new use management.

Order 12 clarifies that fertilizers are out of scope of the regulation.

NOTIFICATION TYPE

Like MEP Order 7, the revision contains three types of notifications:

- regular notification—for new substances imported or manufactured in volumes greater than 10 MT a year;
- simplified notification—substances manufactured or imported in volumes between one and 10 MT a year (under MEP Order 7, these substances require regular notification); and

- record filing notification—this is for new substances in volumes of less than one MT, polymers that meet the “2% rule”, and polymers of low concern.

Record filing notification does not require explicit ministry approval. Companies can begin production, import, or use as soon as they have submitted the necessary information and documents to the MEE.

The small volume exemption for substances used for R&D purposes in volumes under 100kg contained in the draft version of the revised regulation has been removed from the final version.

The revised regulation also extends the notification provisions from manufacturers and importers to downstream users, which can notify new substances when:

- they use exempt substances (pharmaceuticals or pesticides) for industrial uses; or
- they use an existing substance in a different way to the use specified in the inventory.

In addition, foreign traders exporting new substances to China can also carry out the notification process. However, they must appoint local representatives to submit new substance notifications and the representatives must assume legal responsibilities on behalf of the foreign trader or manufacturer.

CBI PROTECTION

The revised regulation allows a maximum protection period of confidential business information (CBI) for new substances of five years, which cannot be extended.

For all substances listed on the inventory with CBI claims, the protection period will end on December 31, 2025. This means that the IECSC will become a full public inventory from January 1, 2026.

INCLUSION ON EXISTING INVENTORY

Under Order 12, notified new substances will be added to the IECSC five years from the date of approval.

Only new substances notified with regular notifications qualify for IECSC listings. As with the current MEP Order 7, simplified notification substances are not added onto the inventory and always remain as new substances.

ANNUAL REPORTING

The new regulation reduces the requirements for annual reporting. Under MEP Order 7, companies are required to submit annual reports for the majority of new substances, regardless of their hazard or risk.

Under the new regulation, companies are only required to submit annual reports for those new substances meeting PB, PT, or BT criteria or highly hazardous substances and such requirements will be specified in the registration certificate.

The MEE is currently working on guidance for new chemical substance notification, which will provide more information on data requirements and detailed notification procedures.

START PREPARING

Experts advise companies to familiarize themselves with the registration requirements under China’s revised regulation on new chemicals ahead of its implementation on January 1.

Lisa Zhong, product registration and compliance expert at the China National Chemical Information Center (CNCIC) told *Chemical Watch* there are big changes in the revised regulation compared to MEP Order 7.

“The good news is that for new chemical manufacturers or importers, the registration types have been simplified and adjusted, and the data requirements are lower than before. But for persistent, bioaccumulative and toxic substances (PBTs), or highly hazardous chemicals, the authorities have added management control requirements,” Zhong said.

Also, while the data requirements have been greatly reduced after the revision of the regulations, the requirements for data quality are more stringent. “More attention will be paid to risk prevention and control, especially for highly hazardous substances,” Zhong said.

PUBLICATION OF GUIDANCE DOCUMENTS

Zhong advised companies to pay close attention to the data requirements when they are published in the guidance documents.

In the meantime, she noted that companies could begin preparing a plan for the studies they might need to conduct for substance registrations.

As with previous regulations, the MEE will publish additional technical guidance for new chemical substance notification, which will provide more information on data requirements and detailed notification procedures.

“It should be published before MEE Order 12 enters into force, but it is not clear if it will be in the next month or in several months. But I know the authorities are working full speed on it,” said Heng Li, senior associate at law firm Mayer Brown

REMOVAL OF LOW VOLUME EXEMPTION

The low volume exemption for substances used for R&D that was previously included in the drafts of the regulation and details on other notification types has disappeared from the final version, but could be included in the guidance,” Zhong said.

Li added that a low volume exemption for new and existing substances is included in the draft Environmental Risk Assessment and Control Regulation for Chemical Substances (Erac), which will form the overarching framework for governing new and existing chemicals when it is approved. While Erac is a much higher level regulation than MEE Order 12, it will not replace its authority over new chemicals. Erac will provide the general requirements for the regulation of new substances while MEE Order 12—along with its soon-to-be-published guidance documents —will provide the detail.

Argentina-Perú: plant-based emulsifiers

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

Leslie Kleiner

I recently learned about new research on soybean okara derivatives that yield plant-based emulsifiers. To learn more about research in this area, I held a discussion with Professor Dario Cabezas, who is a member of the National Scientific and Technical Research Council of Argentina, a professor at the Universidad Nacional de Quilmes, Argentina, and an Associate Research Scientist at Universidad Nacional Agraria de La Molina, Perú.

Q: What is soybean okara?

Soybeans are legumes that allow production of different foods, such as flour, protein isolates and concentrates, oils, lecithin, and fermented products like tofu. Soybean okara arises as an insoluble byproduct of many food products made with soy, most commonly coming from tofu and protein isolate production. Since soybean okaras result from different industrial processes, their extraction yields a varied composition. In my research, we focus on soybean okara arising from traditional processes used to produce isolated soybean protein (ISP). In this sense, defatted soybean flour undergoes an alkaline extraction (pH 8–9) for the extraction of reserve proteins. The insoluble residue from this extraction contains approximately 40% of the dry solids from the raw material, and accounts for approximately 15% of the protein content entering the process. This is generally later dried and sold as a protein source for animal feed.

Q: What are additional potential applications of soybean okara?

Because soybean okara retains a high content of insoluble proteins and high-molecular-weight polysaccharides (dietary fiber), it could potentially be used as is or in a derived form in food applications. In recent years, our group has been investigating various strategies to obtain specific okara fractions for use as emulsifiers and as dough-conditioners in gluten-free products.

Q: Are the polysaccharides within the fraction also used as emulsifiers?

It is possible to extract a fraction of the soluble polysaccharides using aqueous extraction methods (acid conditions, high-temperature, and pressure). This fraction is called SSPS (soluble soybean polysaccharide) and is commercially produced at an industrial scale (the method for doing so is patented by the Fuji Oil Company) [1]. SSPS contains homogalacturonans and branched rhamnogalacturonans, both of which contain galactans and arabinans, along with 6–8% protein content, depending on the extraction method that is used. This composition yields good emulsification properties; however, the process of making this fraction produces a whole new insoluble residue which we named ISPS (insoluble soybean polysaccharides). Our team has been studying potential uses for ISPS, and we recently published a paper about how this fraction and its modified versions have good emulsification and stabilization properties for oil-in-water (O/W) emulsions [2].

Q: What modifications were made to ISPS and why?

Both okara and ISPS have an elevated content of polysaccharides, proteins, and glycoproteins. We treated the ISPS samples with high-pressure homogenization and/or high-intensity ultrasound at various stages during the extraction process. These treatments yielded fractions with various compositions and functional properties (e.g., interfacial properties, absorption, and water retention capacity).

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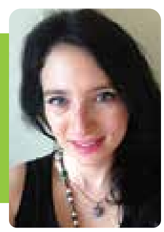
Most importantly, these treatments allow the protein structures to unfold. This promotes interfacial phenomena and reduces the particle size of the fibrous structure, thereby increasing the absorption and water retention, as well as the viscosity of the system in which they are used.

Q: What are potential applications of the modified ISPS?
Given the important role of emulsions in the food industry, research on polysaccharides as plant-based emulsifiers has grown. The specific functional properties of these products would provide plant-based alternatives to synthetic emulsifiers and stabilizers, such as gums. Based on our work, we expect various applications within the food industry, including food emulsions, gluten-free products, and non-dairy beverages. Furthermore, we are currently applying processes similar to those we used to produce soy-based emulsifiers and using them to create emulsifiers from various pseudo-cereals. This work is being carried out in cooperation with researchers of two Argentinean Universities (Universidad Nacional de La Plata, and Universidad Nacional de Lanús) and the Universidad Agraria de La Molina (Perú).

Latin America Update is produced by Leslie Kleiner, a senior research scientist and contributing editor of *Inform*.



Meet Chibuike Udenigwe

Member Spotlight is a regular column that features members who play critical roles in AOCS.

PROFESSIONAL

What's a typical day like for you?
Every day is different for me, but the absolute constant is my two to three trips to the coffee shop. Perhaps it goes without saying that I am a night owl.

My favorite part of my job is…
The favorite part of my job is doing research on proteins while simultaneously teaching, mentoring, and preparing students for their future careers.

Flash back to when you were 10 years old. What did you want to be when you grew up?
A physician. It was the popular choice at the time for students with good grades. But later in my junior secondary school, I dabbled in writing, crafting, comic book drawing, sewing, and farming. At the same time, I constructed electronic appliances for fun and thought about pursuing a career in engineering. I also wanted to follow my father's footsteps to become a mathematician.

Why did you decide to do the work you are doing now?
I come from a family of teachers, lived in a school environment for most of my life, and fell in love with teaching and research early as an undergraduate student in Nigeria. Moreover, the dedication and enthusiasm showed by some of my teachers definitely influenced my choice of career path.

I learned the fundamentals of conducting original research as an undergraduate student. After moving from biochemistry (BSc) to chemistry (MSc), I ended up in the lab of Prof. Rotimi Aluko at the University of Manitoba for my doctoral work. It was then that I developed a deep interest in food proteins and peptides. This interest continued through my brief postdoc with Prof. Rickey Yada at the University of Guelph and expanded significantly after I started my independent research group in 2012.

Is there an achievement or contribution you are most proud of? Why?
I have received a number of international recognitions (including the AOCS Young Scientist Research Award in 2018) for work on food proteins and peptides. I am proud of this because it reflects the collective achievement of my research group and productive collaboration with colleagues over the years.

Fast facts

Name	Chibuike Udenigwe
Joined AOCS	2009
Education	Ph.D. in food and nutritional sciences from the University of Manitoba (Canada)
Job title	Associate Professor and University Research Chair, School of Nutrition Sciences
Employer	University of Ottawa (Ottawa, Ontario, Canada)
Current AOCS involvement	Vice Chair, Protein and Co-products Division

PERSONAL

How do you relax after a hard day of work?
I hang out with my wife, Ogochukwu, and our three young children. Ogo and I also follow a number of TV series. When possible, I like to play soccer and ping pong. Also, as the family entertainer, I love to sing and dance for relaxation.

What is the most impressive thing you know how to do?
I play hand ocarina, which I learned as a kid three decades ago during regular family vacations to our village. I am now trying to pass this skill to our kids, but it seems harder to teach than I remember.

What skill would you like to master?
Playing the guitar.

What are some small things that make your day better?
Hugs and kisses from my wife and kids, some cups of good coffee, and long bus rides to work to clear my head (and save the environment).

PATENTS

Removing toxins from edible fats and oils

Alasti, P., Artisan Industries, Inc., US10472589, November 12, 2020

A method for removing FFAs and toxins from edible oils, without requiring short path distillation and its attendant high temperatures and high loss of product, includes preheating a crude or refined edible oil input stream, having a toxic material content of at least about 1 PPB, to a temperature of about 400–450°F, and introducing the preheated edible oil stream to the top of a vertical stripper column operating at a pressure of about 0.1–3 Torr, typically about 2 Torr. The downward flowing edible oil stream in the stripper is stripped by superheated steam flowing in a countercurrent direction up through the stripper column. Refined and deodorized edible oil having a toxic material content of less than about 500 PPT, and typically as low as about 1 PPT, and at most about 0.2% by weight FFAs, is removed from the stripper.

Infant nutrition for improving fatty acid composition of brain membranes

Van Der Beek, E.M., *et al.*, N.V. Nutricia, US10548869, February 4, 2020

The present invention relates to infant nutrition, in particular to infant nutrition comprising special lipid globules for improvement of the fatty acid composition in brain membranes.

Cosmetic compositions and methods providing enhanced penetration of skin care actives

Gujraty, K.V., *et al.*, The Procter & Gamble Company, US10549129, February 4, 2020

A cosmetic composition suitable for topical application is provided. The cosmetic composition comprises: glycerin; a lipid bilayer structurant with a glyceryl headgroup; a penetration enhancer; and a skin care active. The penetration enhancer increases the amount of active that enters skin when the composition is topically applied, while the glycerin and lipid bilayer structurant with glyceryl headgroup work together with lipid bilayers of the skin to impede progress of active through the skin.

Process for the manufacture of diesel range hydrocarbons

Myllyoja, J., *et al.*, Neste OYJ, US10550332, February 4, 2020

The invention relates to a process for the manufacture of diesel range hydrocarbons wherein a feed is hydrotreated in a hydrotreating step and isomerised in an isomerisation step, and a feed comprising fresh feed containing more than 5 wt% of free fatty acids and at least one diluting agent is hydrotreated at a reaction temperature of 200–400°C., in a hydrotreating reactor in the presence of catalyst, and the ratio of the diluting agent/fresh feed is 5–30:1.

Multi-surfactant systems comprising lauric arginate ethyl ester and fatty acid

Catchmark, J., *et al.*, The Penn State Research Foundation, US10550353, February 4, 2020

Multi-surfactant systems where two or more surfactant molecules are coupled to control the spatial distribution of polar groups of the combined surfactant molecules are disclosed. The system can be implemented by an aqueous medium including an associate charge constant surfactant and charge variable surfactant. The charge variable surfactant has at least one neutral end group at one pH value of the medium and at least one either an anionic polar group or a cationic polar group at a different pH value of the medium. The charge constant surfactant has at least one, and preferably two or more groups that does not change charge at the one or different pH values of the aqueous medium. The multi-surfactant system can be coupled or connected to the surface of a substrate where the arrangement of the two or more coupled surfactant molecules control the polarity of the substrate surface.

Roofing product including bio-based asphalt mixture and methods of making the roofing product and the roofing-grade asphalt mixture

Hong, K.C., *et al.*, Certainteed Corp., US10550574, February 4, 2020

A method of forming an asphalt mixture includes mixing a polyol with a bio-source material to form a bio-asphalt. The method can further include mixing the bio-asphalt with a bitumen source different from the bio-asphalt to form an asphalt mixture. The bio-source material can include an oil, such as a vegetable oil, an animal fat, or any combination thereof. The bitumen source can include a petroleum-based asphalt. The method can further include adding a modifier, such as a fatty acid, a polycarboxylic acid, a polyacrylic acid, a polyacrylate comprising a copolymer, or any combination thereof. Moreover, a roofing grade asphalt mixture includes a bio-asphalt. The bio-asphalt includes an alkyd, wherein the alkyd is a reaction product of a polyol and a bio-source material. The roofing grade asphalt mixture further includes a bitumen source material and particles.

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JAOCS

Chemical compositions of walnut (*Juglans regia* L.) oils from different cultivated regions in China
Wang, X., *et al*.
http://dx.doi.org/10.1002/aocs.12097

A sustainable process for the production of varnishes based on pelargonic acid esters
Ruffo, F., *et al*.
http://dx.doi.org/10.1002/aocs.12200

Effect of moisture and heat treatment of corn germ on oil quality
Huang, J., *et al*.
http://dx.doi.org/10.1002/aocs.12032

Highly efficient synthesis of hydrophilic phytosterol derivatives catalyzed by ionic liquid
He, W., *et al*.
http://dx.doi.org/10.1002/aocs.12024

Plant RuBisCo: an underutilized protein for food applications
Udenigwe, C., *et al*.
http://dx.doi.org/10.1002/aocs.12104

Lipids

Analytical method for diacylglycerol kinase ζ activity in cells using protein myristoylation and liquid chromatography–tandem mass spectrometry
Sakane, F., *et al*.
http://dx.doi.org/10.1002/lipd.12201

Biosynthesis of jasmonates from linoleic acid by the fungus *Fusarium oxysporum*. Evidence for a novel allene oxide cyclase
Oliw, E., *et al*.
http://dx.doi.org/10.1002/lipd.12180

Leucine, palmitate, or leucine/palmitate cotreatment enhances myotube lipid content and oxidative preference
Vaughan, R., *et al*.
http://dx.doi.org/10.1002/lipd.12126

Lipid Profile and glycerophospholipid molecular species in two species of edible razor clams *Sinonovacula constricta* and *Solen gouldi*
Zhou, D., *et al*.
http://dx.doi.org/10.1002/lipd.12153

Suppression of lysophosphatidylcholine-induced human aortic smooth muscle cell calcification by protein kinase A inhibition
Kang, J., *et al*.
http://dx.doi.org/10.1002/lipd.12178

Journal of Surfactants and Detergents

Conductometric probe analysis of the effect of benzyldimethylhexadecylammonium chloride on the micellization behavior of dodecyltrimethylammonium bromide in aqueous/urea solution: investigation of concentration and temperature effect
Hoque, M., *et al*.
http://dx.doi.org/10.1002/jsde.12011

Interaction of metal ion-coordinated dipeptide complex and ninhydrin in the alkanediyl-α,ω-bis-type gemini surfactant system
Kumar, D., *et al*.
http://dx.doi.org/10.1002/jsde.12340

Renewable surfactants for biochemical applications and nanotechnology
Martin, P., *et al*.
http://dx.doi.org/10.1002/jsde.12216

A zwitterionic surfactant bearing unsaturated tail for enhanced oil recovery in high-temperature high-salinity reservoirs
Hussain, S., *et al*.
http://dx.doi.org/10.1002/jsde.12024

Extended surfactants including an alkoxylated central part intermediate producing a gradual polarity transition—a review of the properties used in applications such as enhanced oil recovery and polar oil solubilization in microemulsions
Salager, J., *et al*.
http://dx.doi.org/10.1002/jsde.12331

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

Review Articles

EAT LOQ Valorization of bio-residuals in the food and forestry sectors in support of a circular bioeconomy: a review

Gregga, J.S., *et al.*, *J. Clean. Prod.*, In Press, 122093, 2020, https://doi.org/10.1016/j.jclepro.2020.122093.

This literature review focuses on valorization of bio-residuals from the brewery, dairy, slaughterhouse, and forestry sectors. Bio-residuals are organic wastes, side streams, or residues that remain after processing a biological raw material. These under-utilized resources have the potential to support circular bioeconomies, given they can be valorized through viable value chains. We analyzed 57 publications with findings related to bio-residuals valorization value chains in the categories of resource procurement, transport and handling, transformation and processing, valorization and market, and end use. Contextual drivers, including policy and governance, business strategies, economics, demand, innovation, research, and development, and actors and networks, were analyzed. We categorized the value chains for each sector and then identified the push-pull factors and their influence on bio-residual value chains. The dairy industry has a well-developed modular value chain for bio-residuals, with myriad products from whey being pulled by market demand. The slaughterhouse industry resembles the dairy industry but has greater barriers for valorization of animal by-products and so less market pull, leading to a more conglomeration of rendering operations and a captive value chain. In contrast, valorization of brewers spent grains (BSG) has been slow to develop, due mainly to low supplier capability, and the BSG value chain is dominated by use of unprocessed BSG as animal feed. The forestry industry has been slow to invest in technological and market capabilities for valorizing residuals due to weak market pull, high capital needs, and risk-adverse strategies among the few incumbent firms. As a result, the value chain for forest residues is still mainly hierarchical and rather undeveloped, yet the recent entry of many new firms competing for biomass for a variety of end products has created a shift toward a relational value chain that may develop into a greener and more complex industrial symbiosis production model. Multiple factors shape the value chains for bio-residual products, with each sector having unique challenges and opportunities related to their value chains. More research on downstream parts of the value chain, such as end-product markets, as well as cross-cutting issues such as governance and regulation, could better promote valorization pathways, creating a market pull rather than just a technology push for bio-residuals.

EAT LOQ Potential utilization of bioproducts from microalgae for the quality enhancement of natural products

Tang, D.Y.Y., *et al.*, *Bioresour. Technol. 304*: 122997, 2020, https://doi.org/10.1016/j.biortech.2020.122997.

Microalgae are autotroph organisms that use light energy to synthesize high-value bioactive compounds, such as polysaccharides, proteins, and lipids. The process of obtaining microalgae-based biomolecules for industrial use starts with the selection and cultivation of a suitable microalgae strain, followed by downstream processing of the biomass (i.e., pre-treatment, harvesting, extraction, and purification). The end products are biofuels and other valuable bioproducts. Nevertheless, low-production yield and high-cost downstream processes are bottlenecks which must be addressed to enable upscaling of extracted compounds from microalgae biomass.

LOQ H&N Valorization of melon fruit (*Cucumis melo* L.) by-products: phytochemical and biofunctional properties with emphasis on recent trends and advances

Gómez-García, R., *et al.*, *Trends Food Sci. Tech. 99*: 507–519, 2020, https://doi.org/10.1016/j.tifs.2020.03.033.

Melon (*Cucumis melo* L.) processing generates a high amount of peels and seeds. This review summarizes information about the bioactive compounds in the melon fruit, as well as the nutritional properties it presents as a functional food, with a focus on its by-products (pulp, seed, and peel). Extracts of melon fruit, mainly from the peel, have been shown to possess phytochemical compounds that exhibit antioxidant, antimicrobial, antidiabetic, antiviral, anti-inflammatory, anti-hypoglycemia, and anti-proliferative effects in various *in vitro* and *in vivo* tests. However, it is necessary for further analyze the nutritional and functional potential of these by-products, identify the therapeutic and clinic mechanisms involved, and to develop its industrial process as functional or nutraceutical food products.

Original Articles

ANA Gas chromatography chemical ionization mass spectrometry and tandem mass spectrometry for identification and straightforward quantification of branched chain fatty acids in foods

Wang, D.H., *et al.*, *J. Agric. Food Chem. 68*: 4973–4980, 2020, https://doi.org/10.1021/acs.jafc.0c01075.

Fatty acid analysis of food lipids containing branched chain fatty acids (BCFAs) are complex because of unavoidable gas chromatography (GC) co-elution. We demonstrate a method for convenient quantitative GC coupled to novel solvent-mediated chemical ionization (CI) mass spectrometry (MS) that enables resolution of co-eluting peaks by mass. The relevant masses yield uniform responses for C14–20 normal fatty acids and BCFAs, eliminating the need for rare purified BCFA standards essential for unpredictable responses, as for electron ionization (EI). CI–tandem mass spectrometry analysis of MH+ yields fragments characteristic of the branch position. Application of the measurement to BCFAs in salami samples demonstrates consistent results for the novel method and EI–MS. A higher proportion of C17–18 BCFAs was found in beef compared to milkfat, possibly indicative of fatty acid elongation, endogenous in the beef animal. This method enables straightforward structure elucidation and quantification of food BCFAs and similar chain length normal fatty acids without purified standards.

ANA H&N LOQ PRO Camu-camu seed (*Myrciaria dubia*)—from side stream to an antioxidant, antihyperglycemic, antiproliferative, antimicrobial, antihemolytic, anti-inflammatory, and antihypertensive ingredient

Fidelis, M., *et al.*, *Food Chem. 310*: 125909, 2020, https://doi.org/10.1016/j.foodchem.2019.125909.

Camu-camu (*Myrciaria dubia*) seeds are discarded without recovering the bioactive compounds. The main aim of this study was to optimize the solvent mixture to extract higher total phenolic content and antioxidant capacity of camu-camu seeds. The optimized solvent system increased the extraction of phenolic compounds, of which vescalagin and castalagin were the main compounds. The optimized extract displayed antioxidant capacity measured by different chemical and biological assays, exerted antiproliferative and cytotoxic effects against A549 and HCT8 cancer cells, demonstrated antimicrobial effects, protected human erythrocytes against hemolysis, inhibited α-amylase and α-glucosidase enzymes, and presented *in vitro* antihypertensive effect. The optimized extract also inhibited human LDL copper-induced oxidation *in vitro* and reduced the TNF-α release and NF-κB activation in macrophages cell culture. Thus, the use of camu-camu seed showed to be a sustainable way to recover bioactive compounds with *in vitro* functional properties.

ANA H&N LOQ PRO An effective method for the semi-preparative isolation of high-purity anthocyanin monomers from *grape pomace*

Zhao, X., et al., Food Chem. 310: 125830, 2020, https://doi.org/10.1016/j.foodchem.2019.125830.

Grape (*Vitis vinifera* L.) pomace, the residue of red wine production, is a good source material for production of anthocyanins. In this study, an effective and simple method for semi-preparative isolation of anthocyanins from grape pomace was developed. Ultrasonication with acidified MeOH was used to extract anthocyanins, with 56.15 mg total anthocyanins being obtained from 50 g grape pomace. Crude extracts were purified by XAD-7HP column chromatography, followed by isolation of the anthocyanin mixtures using semi-preparative HPLC, and subsequent identification of anthocyanin monomers by HPLC-DAD-MS/MS. Fourteen anthocyanins were isolated with high purities (≥90%), among which were non-acylated and acylated anthocyanins, and their cis and trans isomers. It is believed this is the first time that nearly all primary anthocyanin monomers in grapes have been isolated simultaneously using a single-step semi-HPLC procedure. The findings of this study will contribute to further research on anthocyanin monomers and profitable utilization of grape pomace.

ANA H&N Comparison of two *Polygonum chinense* varieties used in Chinese cool tea in terms of chemical profiles and antioxidant/anti-inflammatory activities

Wu, Y., *et al., Food Chem. 310*: 125840, 2020, https://doi.org/10.1016/j.foodchem.2019.125840.

Despite the extensive use of *Polygonum chinense* (PC) as a detoxifying ingredient of Chinese cool tea, the efficacy of different PC varieties remains underexplored. Herein, we compare the chemical profiles and antioxidant/anti-inflammatory activities of the aqueous extracts of two PC varieties, namely *P. chinense* var. chinense (PCC) and *P. chinense* var. hispidum (PCH). Ultra-high-performance liquid chromatography coupled with quadrupole time-of-flight mass spectrometry (UHPLC-QTOF-MSMS) and multivariate analysis are used to rapidly identify extract components, while DPPH radical scavenging and xylene-induced mice ear edema assays are used to evaluate antioxidant and anti-inflammatory activities, respectively. Correlation analysis reveals that ellagic acid and quercitrin contents are positively correlated with the magnitude of the anti-inflammatory effect, and the adopted technique is concluded to allow for the rapid discrimination of PC varieties used in Chinese cool tea formulations.

BIO Production of squalene in *Bacillus subtilis* by squalene synthase screening and metabolic engineering

Song, Y., *et al.*, *J. Agric. Food Chem. 68*: 4447–4455, 2020, https://doi.org/10.1021/acs.jafc.0c00375.

Squalene synthase (SQS) catalyzes the conversion of two farnesyl pyrophosphates to squalene, an important intermediate in between isoprene and valuable triterpenoids. In this study, we have constructed a novel biosynthesis pathway for squalene in *Bacillus subtilis* and performed metabolic engineering aiming at facilitating further exploitation and production of squalene-derived triterpenoids. Therefore, systematic studies and analysis were performed including selection of multiple SQS candidates from various organisms, comparison of expression vectors, optimization of cultivation temperatures, and examination of rate-limiting factors within the synthetic pathway. We were, for the first time, able to obtain squalene synthesis in *B. subtilis*. Furthermore, we achieved a 29-fold increase of squalene yield (0.26–7.5 mg/L) by expressing SQS from *Bacillus megaterium* and eliminating bottlenecks within the upstream methylerythritol-phosphate pathway. Moreover, our findings showed that also ispA could positively affect the production of squalene.

BIO Engineering cell wall integrity enables enhanced squalene production in yeast

Son, S.-H., *et al.*, *J. Agric. Food Chem. 68*: 4922–4929, 2020, https://doi.org/10.1021/acs.jafc.0c00967.

Microbial production of many lipophilic compounds is often limited by product toxicity to host cells. Engineering cell walls can help mitigate the damage caused by lipophilic compounds by increasing tolerance to those compounds. To determine if the cell wall engineering would be effective in enhancing lipophilic compound production, we used a previously constructed squalene-overproducing yeast strain (SQ) that produces over 600 mg/L of squalene, a model membrane-damaging lipophilic compound. This SQ strain had significantly decreased membrane rigidity, leading to increased cell lysis during fermentation. The SQ strain was engineered to restore membrane rigidity by activating the cell wall integrity (CWI) pathway, thereby further enhancing its squalene production efficiency. Maintenance of CWI was associated with improved squalene production, as shown by cell wall remodeling through regulation of Ecm33, a key regulator of the CWI pathway. Deletion of ECM33 in the SQ strain helped restore membrane rigidity and improve stress tolerance. Moreover, ECM33 deletion suppressed cell lysis and increased squalene production by approximately 12% compared to that by the parent SQ strain. Thus, this study shows that engineering of the yeast cell wall is a promising strategy for enhancing the physiological functions of industrial strains for production of lipophilic compounds.

EAT IOP PHO PRO New type of green extractant for oil production: citric acid/citric acid sodium extraction system

Huang, W.-C, *et al.*, *Food Chem. 310*: 125815, 2020, https://doi.org/10.1016/j.foodchem.2019.125815.

Developing green solvents with low toxicity and low energy consumption is an important issue for edible oil production. In this study, a novel extraction system, specifically a citric acid/citric acid sodium mixture, was developed for oil extraction from seed crops. Peanut and pumpkin seeds were used to evaluate extraction efficiency and more than 70% and 57% oils, respectively, were extracted from peanut and pumpkin seeds at 4°C. After extraction, the oils floated on the surface of the solution and could be separated from the solvent system without evaporation. The extraction of edible oils was achieved without the use of toxic chemicals or energy-intensive equipment. This study provided a green and efficient method and showed the potential of the proposed citric acid/citric acid sodium extraction system for production of edible oils from natural sources.

EAT LOQ Valorization of horse chestnut burs to produce simultaneously valuable compounds under a green integrated biorefinery approach

Gullón, P., *et al.*, *Sci. Total Environ. 730*: 139143, 2020, https://doi.org/10.1016/j.scitotenv.2020.139143.

A biorefinery scheme for the valorization of horse chestnut biowastes (a municipal solid waste) into added-value bioactive compounds is proposed. The bur fraction of horse chestnut was evaluated as a novel and cheap renewable feedstock to obtain valuable compounds suitable for use in industrial applications. The integrated valorization scheme comprised an initial hydroethanolic extraction of antioxidant compounds (optimized through surface response methodology), the alkaline delignification of the exhausted solid to obtain a lignin-enriched fraction, and the enzymatic digestibility of the remaining cellulose fraction to produce fermentable sugars. The structural characterization of the extract by FT-IR and TGA was also performed, and the analysis by UPLC-DAD-ESI-MS allowed the tentative identification of eleven antioxidant phenolic compounds. The application of this multiproduct valorization approach led to the production of 13 kg antioxidant extracted compounds, 33.2 kg lignin and 14.5 kg glucose per each 100 kg of horse chestnut burs, which demonstrates the great potential of this residue as a biorefinery substrate.

EAT Organic solid waste biorefinery: sustainable strategy for emerging circular bioeconomy in China

Duan, Y., *et al.*, *Ind. Crops Prod. 153*: 112568, 2020, https://doi.org/10.1016/j.indcrop.2020.112568.

The present study provides a comprehensive review of the status of available biorefinery approaches to managing organic solid waste derived from agriculture, industry, and urban areas. In addition, a techno-economic assessment was used to identify current challenges and gain a future perspective on the sustainability of a circular bio-economy in China. The results demonstrated that diverse kinds of solid waste played an essential role in implementing the biorefinery approach, and that achieving a sustainable circular bio-economy requires coordinated economic, environmental, and social efforts. There is still a huge gap between actual performance and expectations.

H&N Role of maltodextrin and inulin as encapsulating agents on the protection of oleuropein during *in vitro* gastrointestinal digestion

González, E., *et al.*, *Food Chem. 310*: 125976, 2020, https://doi.org/10.1016/j.foodchem.2019.125976.

Olive leaves extract (OLE) was spray-dried with maltodextrin (MD) or inulin (IN) to study the evolution of oleuropein (OE) during *in vitro* gastrointestinal digestion, its bioaccessibility and potential bioavailability. In the case of OLE–MD, OE was partially degraded in gastric and intestinal conditions; whereas in OLE–IN, OE was released under gastric conditions and partially degraded under intestinal conditions. In both cases, the encapsulation of OLE led to higher OE contents at the end of digestion, compared with non-encapsulated OLE, suggesting a protective role of the polysaccharides by the formation of non-covalent polysaccharides–OE complexes. OE bioaccessibility was 10 times higher ($p \leq 0.05$) in OLE–MD and OLE–IN than in non-encapsulated OLE. However, OE potential bioavailability, evaluated by tangential filtration, was not detected. Encapsulation technology and the encapsulant agent used may determine the release of the encapsulated compounds at a specific-site and their effect on health.

H&N Use of dietary components to reduce the bioaccessibility and bioavailability of cadmium in rice

Sun, S., *et al.*, *J. Agric. Food Chem. 68*: 4166–4175, 2020, https://doi.org/10.1021/acs.jafc.0c01582.

Reducing Cd bioavailability in the systemic circulation is an alternative strategy to reduce Cd exposure. The influence of 39 dietary components on Cd bioaccessibility in water or rice was determined using an in vitro gastrointestinal model, following which an *in vivo* bioassay was used to determine the most effective components on Cd bioavailability in rice. The results showed that several components significantly reduced the solubility of Cd (10–98%) in the intestinal phase. Tannic acid, TiO_2, zinc gluconate, $CaCl_2$, and proanthocyanidins were the most effective in decreasing Cd bioaccessibility in rice, with reductions of 93–97, 54–61, 32–49, 24–32, and 11–14%, respectively. Upon adding the dietary components, the reduction rates of the Cd-relative bioavailability (Cd-RBA) were 20–58 and 10–31% in the kidneys and the liver, respectively. The results may have important implications for reducing health risks associated with Cd exposure via consumption of rice.

PRO IOP Extraction of lipids and production of biodiesel from secondary tannery sludge by *in situ* transesterification

Indu, V.K. and S. Thakur, Bioresour. Technol. 11, September 2020, 100446, https://doi.org/10.1016/j.biteb.2020.100446.

This study investigated the effect of different solvent on lipids extraction efficiency and biodiesel production under optimized process parameters from tannery sludge. Results revealed that standard chloroform-methanol method has a higher lipid yield of 22.8% (*w/v*), corresponding to 98.5% (w/v) of lipid extraction efficiency at optimal conditions. The optimized conditions for *in-situ* transesterification procedure were: catalyst concentration of 3% (*v*/v), sludge solid to methanol ratio of 1: 25 (w/v), reaction temperature of 60°C, and time of 12 h, achieving 89.7% yield of biodiesel. Further, the FAME profile of biodiesel analyzed by FT-IR, ^{1}H and ^{13}C NMR, and GC–MS showed a purity higher than 97.12%. The physicochemical properties of 5% blended biodiesel were found to be within the ASTM standards. The results indicate that the production of biodiesel from sludge could be techno-economically viable due to extremely high lipids yield and low-cost of this feedstock.

PRO IOP Continuous production of fatty acid methyl esters and high-purity glycerol over a dolomite-derived extrudate catalyst in a countercurrent-flow trickle-bed reactor

Jindapon, W., *et al.*, *Renew. Energ. 157*: 626–636, September 2020, https://doi.org/10.1016/j.renene.2020.05.066.

Fatty acid methyl esters (FAME), as biodiesel components, were continuously produced via heterogeneously catalyzed transesterification of palm oil with methanol vapor in a countercurrent-flow trickle-bed reactor. Dolomitic rock was used as natural calcium source in the preparation of the calcium oxide-based extrudate catalyst via a physical mixing method. Effects of operating parameters on the FAME yield and the two-phase flow behavior were investigated. The reaction system was characterized by a high mass diffusion resistance at gas-liquid-solid interfaces due to the low solubility of methanol in triglycerides and the high viscos-

ity of oil. Mixing palm oil with commercial grade methyl decanoate, a C10 methyl ester (C10 CME), at a 1:1 mass ratio during the start-up period promoted FAME production. The FAME yield was enhanced by increasing the operating temperature and the methanol flow rate, while operation at a high oil flow rate severely decreased the FAME yield. The concentration of C10 CME, which acted as an emulsifier, in the catalyst bed was crucial to maintain the FAME production stability. In addition to a high FAME yield (ca. 92.3 wt%), the system provided glycerol, obtained without any washing, at a high purity of 93.6 wt%.

PRO IOP Biochemical and kinetic evaluation of lipase- and biosurfactant-assisted *ex novo* synthesis of microbial oil for biodiesel production by *Yarrowia lipolytica,* utilizing chicken tallow

Keerthana, P.R., *et al., Process Biochem.* 95: 17–29, August 2020, https://doi.org/10.1016/j.procbio.2020.05.009.

This study explores the production of biodiesel by utilizing microbial oil, which was procured from *Yarrowia lipolytica,* employing chicken tallow as the carbon substrate. Chicken tallow, yeast extract, and $MgSO_4{\cdot}7H_2O$ were screened for biomass production through Plackett–Burman design. Further, Box–Behnken design analysis was performed, and the optimal concentration of the medium variables was found to be 20 g/L of chicken tallow, 7.0 g/L of yeast extract, and 0.45 g/L of $MgSO_4{\cdot}7H_2O$.The various parameters viz., pH (6), temperature (30°C), RPM (150), inoculum volume (5%, v/v), and C/N ratio (100) were optimized for maximal biomass and lipid yield, and lipid content. Nile red-stained cells were observed for intracellular lipid bodies using fluorescence microscopy, and its fluorescence intensity was measured by the flow cytometer. The dimorphic transition and substrate assimilation of *Y. lipolytica* were analyzed using scanning electron microscopy (SEM), and Fourier transform infrared spectroscopy (FT-IR). Batch kinetic studies revealed the concomitant synthesis of microbial lipid (4.16 g/L), lipase (43 U/mL), and biosurfactant (1.41 g/L). The GC-MS analysis of microbial oil presented the fatty acid profile as oleic acid (49.15%), palmitic acid (29.83%), stearic acid (11.43%), linoleic acid (3.83%), palmitoleic acid (3.77%), and myristic acid (1.32%).