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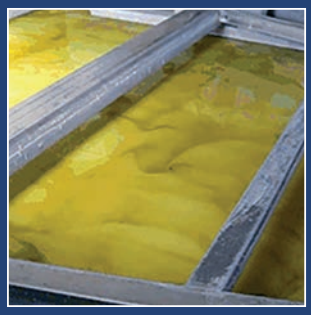

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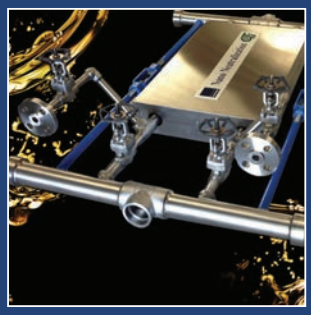

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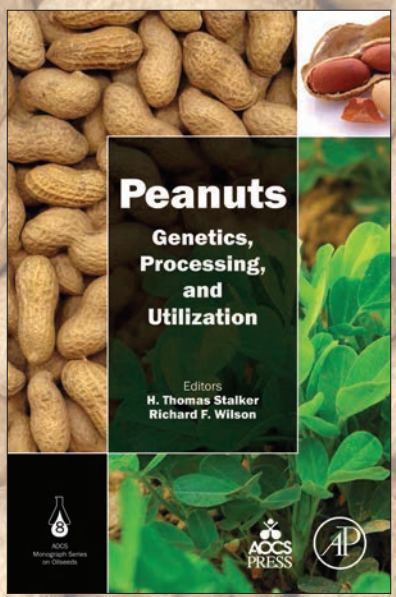

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Red palm oil

Laura Cassiday

For centuries, people on the African continent, including the ancient Egyptians, used red palm oil (RPO) for culinary purposes. Only recently has the minimally processed palm oil been introduced to Western palates, with variable results. Some people find the red-orange hue unappetizing, while others view the color as a welcome reminder of the oil's high carotene content. Like other "exotic" edible oils such as coconut and avocado, RPO has attracted a cult following for its supposed health benefits. Whether or not RPO can make the leap from a niche oil to widespread commercial success depends on substantiation of these health claims and on the versatility of the oil for a variety of food applications.

- **Red palm oil is mildly processed, allowing it to retain beneficial components such as carotenes and antioxidants that are lost in traditional physical or chemical palm oil refining.**
- **Red palm oil has shown promise for combating vitamin A deficiency in some parts of the world. However, other potential health benefits have not yet been well established.**
- **The commercial success of red palm oil depends on consumer acceptance of the red color it typically imparts to foods. Blends with other oils may increase red palm oil's versatility.**

PALM OIL PROCESSING

Palm oil is derived from the fruit of the oil palm tree, primarily the African oil palm *Elaeis guineensis*. In its natural, unprocessed state, palm oil is dark red in color due to a high content of carotenoids, including β-carotene (a vitamin A precursor that gives carrots their color) and lycopene. The oil is also rich in antioxidants, such as vitamin E isomers (tocopherols and tocotrienols), and phytosterols. However, without any processing, crude palm oil (CPO) has limited utility in the kitchen. "Red palm oil in its crude form is very strong tasting. It's very pungent and has a smell like overripe mushrooms. It's not very palatable," says Neil Blomquist, chief commercial officer for Natural Habitats (Rotterdam, The Netherlands), a supplier of organic palm oil from Ecuador and West Africa. "Companies have tried to introduce crude palm oil into the market, but it has not done well because it doesn't taste good, and it's hard to use in the kitchen." In addition, CPO contains free fatty acids (FFA), moisture, trace metals, and other impurities that limit its shelf life.

As a result, most CPO is refined to remove odors, flavors, and impurities, as well as the red color that many consumers find unappetizing. Refined, bleached, and deodorized (RBD) palm oil is bland, odorless, light yellow in color, and semisolid at room temperature, making it an ideal replacement for partially hydrogenated oils in many snack products and baked goods. Before or after refining, palm oil can be fractionated into palm olein (liquid fraction; 70–80% of palm oil) and palm stearin (solid fraction; 20–30%). Palm olein is typically used as a cooking or frying oil, whereas palm stearin can be found in shortenings and butter substitutes. RBD palm oil is now the most widely used vegetable oil in the world, a key component of foods ranging from baked goods to salad dressings to ice cream (Mancini, A., *et al.*, http://dx.doi.org/10.3390/molecules200917339, 2015).

CPO can undergo physical or chemical refining, although physical refining is more common because of CPO's high FFA content. During the deodorization step of physical refining, edible oils are subjected to high

temperatures (250–270°C) and low pressures (3–5 torr) to remove FFA and volatile compounds that affect the oil's odor and flavor. The deodorization step thermally degrades all carotenes, producing a light-colored oil, and strips away some of the tocopherols, tocotrienols, and phytosterols.

SEEING RED

"The key for producing red palm oil is that you have to deodorize the palm oil at a low temperature to avoid thermal destruction of the carotenes," says Wim De Greyt, R&D manager at Desmet Ballestra (Brussels, Belgium), a company that designs and builds edible oil refineries. "If you go for the classical physical refining, then you need a molecular distillation step so that you can strip off the free fatty acids at a deeper vacuum and lower temperature. Alternatively, if you can start from a very good crude palm oil with a low free fatty acid content, you can apply a chemical refining. You remove the free fatty acids with caustic, and then you also do the deodorization step at a lower temperature." Chemical refining, which removes most FFA by reaction with sodium hydroxide, uses a slightly lower-temperature deodorization (235°C or below) than physical refining. The deodorization temperature can be further decreased if the crude oil is low in FFA. "To retain the carotenes, you probably need to deodorize at temperatures below 220°C," says De Greyt.

The Palm Oil Research Institute of Malaysia developed and patented a physical refining process that produces RPO of similar quality to RBD palm oil, but that retains most of the carotenes, vitamin E, and phytosterols of CPO (Table 1; Nagendran, B., *et al.*, http://dx.doi.org/10.1177/156482650002100213, 2000). In the refining process, CPO is treated with phosphoric acid for degumming and with bleaching earth, followed by filtration. Then, the oil is deodorized and deacidified by molecular distillation at low temperature (less than 170°C) and low pressure (less than 100 mtorr). The resulting RPO retains up to 80% of the carotene and vitamin E content of CPO, with less than 0.1% each of FFA, moisture, and impurities. RPO produced by this process is blended with canola oil and marketed as Carotino (Carotino Group, Johor, Malaysia). In addition to liquid cooking and frying oils, Carotino is available as a margarine, shortening, and butter oil (ghee) substitute.

Natural Habitats has taken a different approach to RPO production. "We developed a cold filtration process to neutralize the flavor of red palm oil," says Blomquist. The procedure, which is done under vacuum, removes the phospholipids that carry flavor bodies, as well as moisture and some of the FFA. The cold filtration process, which Blomquist says is not refining *per se*, retains most of the β-carotene and all of the tocopherols and tocotrienols of CPO. "Our process mostly affects the flavor profile of palm oil," says Blomquist. "In fact, we can kind of fine-tune the process. We have about 12 different flavor profiles to choose from."

RPO produced by cold filtration has a higher FFA content (about 3%) than RPO that has been physically refined by molecular distillation (Carotino, 0.1% max). However, Blomquist says that this relatively high level of FFAs has not caused any problems with stability, presumably because of the high natural content of antioxidants in RPO. "We've been guaranteeing a 12-month shelf life from the time the RPO is packed in bulk to the customer, but I think we could extend it," says Blomquist. One of Natural Habitats' major customers is the organic brand

TABLE 1: Levels of minor beneficial components in palm oil

Sample	Carotenes (ppm)	Vitamin E (ppm)	Phytosterols (ppm)
Crude Palm Oil[a]	643	869	210–620
RBD Palm Olein[a]	Nil	561	109–170
Red Palm Olein[b]	513	707	325–365

[a]Sample from palm oil refinery
[b]Red palm olein sample processed by molecular distillation at the Palm Oil Research Institute of Malaysia.

Credit: Adapted from data in Nagendran, B., *et al.*, http://dx.doi.org/10.1177/156482650002100213, 2000.

Nutiva (Richmond, California, USA), which offers RPO, as well as a shortening that is a blend of RPO and coconut oil (Fig. 1).

FATTY ACID COMPOSITION

RPO has the same fatty acid composition as RBD palm oil (Table 2). Like RBD palm oil, RPO contains approximately 50% saturated fat, 42% of which is palmitic acid (16:0) (Kritchevsky, D., 2000). The high saturated fat content makes RPO semi-solid at room temperature and more stable to lipid oxidation than oils that are composed of mainly unsaturated fatty acids. The other major component of RPO, oleic acid, is a monounsaturated fat also present at about 42%. Minor components such as carotenoids, vitamin E, and phytosterols make up only about 1% of RPO.

"The fatty acid profile of palm oil, whether it is red or RBD, is high in saturated fat," says Gijs Calliauw, product development manager at Desmet Ballestra. "Red palm oil has been promoted for its higher content of minor nutritional components such as carotenes, but 99% of it is still just a palm oil with the negative effects that may come with saturated fatty acid consumption. I think you'd be better off eating carrots."

The health effects of saturated fats remain controversial, with some studies linking saturated fat intake to cardiovascular disease risk, whereas others have failed to find an association (Cassiday, L., *Inform*, 2015). In addition, some research indicates that the health effects of saturated fatty acids depend on their chain length. Medium-chain fatty acids, such as the lauric acid (12:0) plentiful in coconut oil, are metabolized more rapidly than long-chain saturated fatty acids, such as the palmitic acid (16:0) abundant in palm oil (Cassiday, L., *Inform*, 2016a). The slower metabolism of long-chain fatty acids may make them more likely to contribute to obesity and cardiovascular disease than medium-chain fatty acids. Thus, some nutritionists consider coconut oil a more healthful dietary choice than palm oil.

Studies of palm oil consumption and cardiovascular risk have uncovered both favorable and unfavorable changes in disease biomarkers (Mancini, A., *et al.*, http://dx.doi.org/10.3390/molecules200917339, 2015). However, in studies where palm oil is compared to other edible oils such as soybean, olive, sunflower, and canola, no substantial differences in human lipid serum profiles have been observed. Animal studies have even indicated an antithrombotic effect of palm oil. Although RPO may contribute beneficial carotenes and antioxidants that reduce cardiovascular risk, as will be discussed later, most of these studies were conducted using RBD palm oil, suggesting that the fatty acid composition of palm oil in general may not be particularly damaging to cardiovascular health.

TABLE 2: Fatty acid composition of red palm oil

Fatty Acid	Content (%)
14:0 (myristic)	0.8
16:0 (palmitic)	42.0
18:0 (stearic)	5.1
18:1 (oleic)	42.0
18:2 (linoleic)	10.0
Total	99.9

Credit: Data from Kritchevsky, D., *Food Nutr. Bull. 21*, 182–188, 2000.

One possible explanation is the stereospecific positioning of palmitic acid within palm oil triacylglycerides (TAGs). In palm oil TAGs, oleic acid is primarily present in the *sn-2* position, while palmitic acid is found in the flanking *sn-1* and *sn-3* positions. Only 7–11% of the palmitic acid in palm oil is located at the *sn-2* position (May, C. Y., and Nesaretnam, K., http://dx.doi.org/10.1002/ejlt.201400076, 2014). In contrast, in animal fats palmitic acid or stearic acid is usually at the *sn-2* position. Seventy percent of the palmitic acid in lard is present at the *sn-2* position. This stereospecific positioning is thought to play a role in fatty acid absorption and metabolism, and perhaps cardiovascular disease risk (Mancini, A., *et al.*, http://dx.doi.org/10.3390/molecules200917339, 2015). Indeed, the atherogenicity of different TAGs has been linked to the degree of saturation of the fatty acid located at the *sn-2* position.

Although the healthfulness of the fatty acid profile of palm oil is controversial, minor components in RPO may reduce its cardiovascular risk compared with RBD palm oil. Some studies have found that the tocopherol-rich fraction (TRF) of red palm oil reduces serum cholesterol levels in humans, whereas others have not (Kritchevsky, D., 2000). In an animal study, rats fed diets high in RPO showed a reduced low-density lipoprotein (LDL) cholesterol level and a decreased ratio of total cholesterol to high-density lipoprotein (HDL) cholesterol compared with rats fed RBD palm oil or vitamin E-stripped palm oil (Kamisah, Y., *et al.*, *Pakistan J. Nutr.*, 2005). Rabbits fed RPO had a reduced severity of cholesterol-induced atherosclerosis than rabbits consuming RBD palm oil (Kritchevsky, D., 2000). Much more research is needed to determine whether minor components of RPO reduce cardiovascular risk compared with RBD palm and other edible oils.

FIG. 1. Nutiva brand red palm oil is produced by a cold filtration process. Credit: Nutiva

CAROTENOIDS

Carotenoids are fat-soluble pigments found in fruits and vegetables. Carotenoids that contain oxygen in their structure are known as xanthophylls, whereas those that lack

oxygen are called carotenes. Some carotenoids, such as α- and β-carotene, are converted by the body into retinol, or vitamin A_1. β-carotene has about twice the vitamin A activity of α-carotene (Nagendran, B., *et al.*, http://dx.doi.org/10.1177/156482650002100213, 2000). Some carotenoids can act as antioxidants by scavenging oxygen and peroxyl radicals.

CPO is the world's richest natural plant source of carotenoids, containing about 15 times more retinol equivalents than the same weight of carrots (Benadé, A. J., 2003). The carotenoids in RPO are primarily β-carotene (48.2%) and α-carotene (38.9%), with smaller amounts of 11 other carotenoids including lycopene, phytoene, and phytofluene.

Studies of the effects of β-carotene supplementation on cardiovascular disease have produced mixed results (Benadé, A. J., 2003). Some studies indicate that carotenes can inhibit the proliferation of certain types of cancer cells. But by far the best substantiated health benefits of carotenes are in preventing vitamin A deficiency and associated skin and eye diseases.

As a rich source of carotenes, RPO has been investigated as a fortification strategy to combat vitamin A deficiency in the developing world. The highest prevalence of vitamin A deficiency occurs in south Asia and sub-Saharan Africa, where 30–40% of preschool children are at an increased risk of poor health or death due to vitamin A deficiency (Benadé, A. J., 2003). In one study, researchers provided sweet snacks containing RPO to Indian schoolchildren, which increased their serum retinol levels. The researchers estimated that if RPO shortening was widely used in baked goods, it could supply 46–70% of the recommended daily allowance (RDA) of vitamin A in children aged 7–10 years.

In another study, researchers examined the effects of RPO supplementation during pregnancy on maternal and neonatal vitamin A status (Radhika, M. S., *et al.*, 2003). The double-blind, randomized controlled trial assigned 170 pregnant Indian women (16–24 weeks gestation) to: 1. a group receiving RPO containing 1 RDA (2,400 micrograms) of β-carotene per day, or 2. a control group receiving an equivalent amount of groundnut oil. At 34–36 weeks gestation, women in the RPO group had significantly higher levels of serum retinol and significantly lower incidences of vitamin A deficiency and anemia. After delivery, the infants of mothers in the RPO group likewise had higher levels of serum retinol in their cord blood than babies born to the control group.

TOCOPHEROLS AND TOCOTRIENOLS

As vitamin E isomers, tocopherols and tocotrienols are potent antioxidants that confer oxidative stability to RPO. Researchers have detected five vitamin E isomers in RPO: α- and γ-tocopherol; and α-, γ-, and δ-tocotrienols. Approximately 70% of the vitamin E in RPO is in the form of tocotrienols, which are more potent antioxidants and are thought to confer

greater health benefits than tocopherols (Cassiday, L., 2013). A number of beneficial health effects for both tocopherols and tocotrienols have been reported in the literature, including antitumor and antithrombotic properties and enhancement of the immune response (Kamisah, Y., *et al.*, *Pakistan J. Nutr.*, 2005). Tocotrienols have cholesterol-lowering activity, possibly due to their inhibition of HMG CoA reductase, the rate-limiting enzyme in cholesterol biosynthesis.

OTHER COMPONENTS

Phytosterols are plant steroid compounds that have been shown to lower plasma LDL cholesterol. RPO has a higher phytosterol content, including β-sitosterol, campesterol, and stigmasterol, than RBD palm oil (Nagendran, B., *et al.*, http://dx.doi.org/10.1177/156482650002100213, 2000). RPO also contains ubiquinones, primarily coenzyme Q_{10}, a potent antioxidant. Squalene, an antioxidant with antitumor activity in animal models, is present at trace amounts. RPO also contains polyphenols, including phenolic acids and flavonoids, with antioxidant activity.

RED-DY OR NOT?

In 2013, US television personality Dr. Oz declared that RPO "may very well be the most miraculous find of 2013." Perhaps as a result of this publicity, RPO has been showing up in an increasing number of health food stores, and even in some large supermarket chains. But according to Calliauw, RPO remains very much a niche oil. "The vast majority of the big palm oil producers don't put red palm oil out," he says. "Desmet Ballestra does not receive many requests to design refining plants specifically for the production of RPO. Most palm oil refining plants are not even able to do it."

Calliauw sees the red color of RPO as the primary impediment for widespread consumer acceptance. "The big fast-food companies typically fry in palm oil, but I doubt they would ever use red palm oil," he says. "The red color is actually something you want to get rid of because the average consumer doesn't like the appearance, nor appreciate the perceived health benefits. For a whole lot of applications, red palm oil would not be suitable just because of the color."

Blomquist agrees that color has been an issue for consumers. In an attempt to mitigate this problem, Natural Habitats tested some blends of regular palm olein and RPO olein as frying oil. "The blend actually turned the potato chips and corn chips a really beautiful darker yellow color," he says. "Personally, I think RPO has potential in a blend like that, or in a blend with high-oleic sunflower oil." A blend with another oil would also reduce the cloudiness that can be a problem for single-fractionated palm olein. In addition, using a blend of RPO and a high-oleic oil would reduce the amount of saturated fat compared to pure RPO, which could help with marketing. "I think that would make a really great frying oil for snacks," says Blomquist.

Although RPO contains beneficial components not present in RBD palm oil, it could lack two detrimental ones: 3-monochloropropane-1,2-diol (3-MCPD) esters and glycidyl esters. These process contaminants are formed during the high-temperature deodorization of palm oil (Cassiday, L., 2016b). "The hot topic in palm oil refining today is the MCPD and glycidyl esters issue," says De Greyt. "Red palm oil is, almost by definition, low in glycidyl esters and may also contain less 3-MCPD esters because it is more mildly refined. So maybe that could cause a renewed interest in red palm oil."

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AOCS LAB PROFICIENCY PROGRAM

Improving Quality

KAREN LETOURNEAU

Technical Programs Manager, POS Bio-Sciences, Saskatoon, Saskatchewan, Canada

Karen Letourneau has worked at POS Bio-Sciences for 26 years and POS Analytical Services has had an AOCS Approved Chemist on staff since 2011. "Being part of the AOCS Lab Proficiency Program really improves the quality of our testing."

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Authenticity of plant oils in the market place

Glenn Norton

- **Analysis of an oil blend prepared for research purposes gave some unexpected fatty acid concentrations.**
- **Upon further investigation, two of the oils used to make the oil blend were not what the vendor portrayed them to be: Although they had been sold as perilla oil and jojoba oil, their fatty acid profiles actually matched that of soybean oil.**
- **In cases where the authenticity of plant oils is critical for research or commercial purposes, buying oils directly from the manufacturers is desirable, and independent verification of authenticity is recommended.**

Consumers, product developers, and researchers rely on product labeling to properly convey product information, including the identity of the product itself. This includes plant oils, regardless of whether they are "essential oils," fragrance oils, or vegetable oils. The authenticity of oils used for cosmetic, food, and industrial applications is another potential area of concern for consumers. In work being performed at Iowa State University (Ames, Iowa, USA) to study the possibility of using various plant oils to produce a drop-in No. 2 diesel fuel replacement, a blend of various plant oils was prepared such that roughly equal proportions of various fatty acids would be present in the feedstock going into the renewable diesel reactor. Perilla oil and jojoba oil were two of the oils selected because of their unusually high concentrations of linolenic acid and gondoic acid, respectively. However, when the oil blend was analyzed to verify its composition, an unexpected fatty acid profile was obtained. Based on the specific fatty acids where the most serious discrepancies occurred, the composition of the perilla and jojoba oils came into question. Work was subsequently performed to verify whether or not those oils were responsible for the discrepancies.

To determine whether the perilla oil or jojoba oil (or both) was the cause of the discrepancy between the actual and theoretical composition of the blended oil, jojoba and perilla oils from two different vendors were obtained. It should be noted that jojoba oil is very unusual since it does not actually contain triglycerides, but is composed instead of long-chain liquid wax esters of fatty acids and fatty alcohols [1]. Nonetheless, it is generally referred to as an oil. The jojoba and perilla oils were subsequently analyzed for their fatty acid distributions using GC-MS. Analyses were performed by Exact Scientific Services Inc. (Ferndale, Washington). For quality assurance purposes, the samples of the jojoba and perilla oils in question were submitted to a second laboratory for fatty acid analyses, and results always agreed to within 2% (absolute) or better between the two laboratories for any given fatty acid.

SOMETHING SUSPICIOUS

Results of the GC-MS analyses on the jojoba and perilla oils are presented in Table 1, along with the fatty acid profiles reported in the literature for those oils. Literature values for jojoba oil are sparse, so this paper serves as an additional source for the fatty acid composition of jojoba oil. Fatty acids that were present at less than 1% in all of the samples are not included in the table, but the listed fatty acids accounted for 96–97% of the fatty acids in each sample. As can be seen by the data, the oils labeled as "Sample 2" had fatty acid profiles that were in excellent agreement with literature values, while the oils labeled as "Sample 1" had fatty acid concentrations that weren't anywhere close to the literature values. Both of the oils labeled as "Sample 1" were from the same vendor.

TABLE 1. Results of fatty acid analyses on jojoba and perilla oils from two different vendors. The jojoba oil and perilla oil labeled as "Sample 1" are from the same vendor.

	Jojoba Oil			Perilla Oil		
Fatty Acid (wt. %)	Sample 1	Sample 2	Literature Values[a]	Sample 1	Sample 2	Literature Values[b]
C16:0	11	1	1–3	11	7	5–9
C18:0	5	0	0	5	2	1–4
C18:1	21	9	5–12	23	18	12–20
C18:2	**53**	**0**	0	**52**	**15**	13–19
C18:3	7	0	0	**6**	**56**	44–65
C20:1	**0**	**71**	66–74	0	0	0
C22:1	0	15	7–19	0	0	0

[a] From Firestone [2] and Perillo and Maestri [3]

[b] From Firestone [2], Sanford et al. [4], and Chempro [5]

The two "Sample 1" oils were not only completely different from the names claimed on their commercial labels, but their fatty acid profiles were also virtually identical, which cannot be correct if there truly was one sample each of perilla and jojoba oil. Oddly enough, both the jojoba oil and perilla oils labeled as "Sample 1" (which came from the same vendor) had essentially the same fatty acid profile as that of soybean oil (see Table 2). However, the GC-MS analyses are not in themselves adequate to conclude that those samples are truly soybean oil. For some types of oils, caution must also be exercised when drawing conclusions about product authenticity based on their fatty acid profiles. One good example is safflower oil.

TABLE 2. Comparison of fatty acid profiles of jojoba oil (Sample 1) and perilla oil (Sample 1) with that of soybean oil

Fatty Acid (wt. %)	Jojoba Oil, Sample 1	Perilla Oil, Sample 1	Soybean Oil (this study)
C16:0	11	11	10
C18:0	5	5	5
C18:1	21	23	24
C18:2	53	52	51
C18:3	7	6	6

Two types of safflower oil are produced, one being high in oleic acid rather than linoleic acid, and the other where the converse is true. Such issues, however, do not apply to perilla or jojoba oil. At the least, the company marketing the products in question lacks adequate quality control procedures. The intent of this paper is not to point fingers at any given distributor, but rather to document the problem encountered and to emphasize the old adage of "let the buyer beware."

Although adulteration or mislabeling of oil products is known to occur, the magnitude of such problems is unknown. Independent oversight on the authenticity of oil products in the market place would bring added confidence to the consumer. In cases where the authenticity of plant oils is critical for research or commercial purposes, buying oils directly from the manufacturers is desirable, and verification of the authenticity of the oils being used is recommended.

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AOCS MEETING WATCH

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

September 11–14, 2017. 17th AOCS Latin American Congress and Exhibition on Fats, Oils, and Lipids, Grand Fiesta Americana Coral Beach Hotel, Cancun, Mexico. http://lacongress.aocs.org.

May 6–9, 2018. AOCS Annual Meeting & Expo, Minneapolis Convention Center, Minneapolis, Minnesota, USA.

October 28–31, 2018. Fabric and Home Care World Conference, Boca Raton Resort & Club, Boca Raton, Florida, USA.

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2018 Kaufmann Memorial Lecture

Call for Nominations

Nominations for the 2018 award must be submitted no later than March 15, 2017.

The 2018 ISF Lectureship Series will be held in conjunction with the 2018 AOCS Annual Meeting & Expo, May 6-9, 2018 in Minneapolis, Minnesota, USA. Organizers are seeking nominations for the Kaufmann Memorial Lecture, sponsored by Deutsche Gesellschaft für Fettwissenschaft (DGF). The Kaufmann Memorial Lecture is given to honor the memory of the founder of the ISF, Hans P. Kaufmann, to recognize his contributions to the science of fats and oils and to the development of international cooperation in the fats and oils community. The awardee will receive a plaque, travel and expense allowance, plus complimentary congress registration.

Nominations should be accompanied by a short curriculum vitae and a brief statement about the merits of the individual being nominated. These materials combined should not exceed two pages in length. Nominations cannot be accepted for persons from the ISF Lectureship Series host country (USA) nor from the country of the previous awardee (China). The awardee must be able to present the lecture as part of the 2018 ISF Lectureship Series.

Send nominations to:

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Optimizing the use of biomass waste through co-pyrolysis

Faisal Abnisa, Shafferina Dayana Anuar Sharuddin, and Wan Mohd Ashri Wan Daud

- Biomass is a renewable resource that can be used to produce liquid fuel via co-pyrolysis.
- Adding plastic or tire wastes to the pyrolysis of lignocellulosic biomass improves the quantity and quality of pyrolysis oil.
- The use of this co-pyrolysis technique can help reduce waste volume as more waste matter is consumed as raw material.

The production of liquid fuel via the pyrolysis of biomass has been a topic of research for four decades. In 1972, the energy crisis shifted researchers' attention to maximizing the production of pyrolysis oil by minimizing the byproducts of char and gases. One of the best uses of pyrolysis was achieved in the 1980s. The technique led to several improvements, such high-yield oil production, and is known today as "fast pyrolysis." Although fast pyrolysis addressed the issue of oil quantity, improving oil quality is a topic that requires further research.

Current research efforts are focused on finding a suitable technique to produce high-grade pyrolysis oil, and exploring new variations of biomass that can be used as feedstock in the pyrolysis process. The oil produced from the pyrolysis of biomass has a high oxygen content and can cause many problems, such as low calorific value, corrosion, and instability. Our research at the University of Malaya in Malaysia, has shown that the technologies used to eliminate oxygen content, such as catalytic cracking and hydrodeoxygenation, are expensive and can cost more than the oil itself. Such improvement technologies could potentially increase production costs due to the need for complicated equipment and additional catalysts, solvents, and hydrogen-donors.

On the other hand, there is one promising technique for producing high-grade pyrolysis oil from biomass that offers simplicity in design and operation. This technique, which can be run without catalysts, solvents, or hydrogen pressure, is called "co-pyrolysis," because it makes use of two or more different materials as feedstock. The mechanisms of co-pyrolysis and normal pyrolysis are almost the same, but published

TABLE 1. Features of co-pyrolysis

Operation condition and reactor	Product yields	Product quality	Advantages
• Temperature range of 400–600°C. • No need to add catalysts, solvents, and hydrogen pressure. • Short hot vapor residence times of less than 2s. • Hot vapor should be maintained at >400°C before it enters the condensation unit. • To achieve a synergistic effect, a fixed bed reactor and auger reactor are recommended for use. • No need for complicated equipment.	• Compared with normal pyrolysis, co-pyrolysis can produce extra liquid yield, typically between 1.42 and 22 wt%. • The yields of char and gas are lower than that of biomass pyrolysis alone.	• Liquid product has potentially decreased oxygen levels, reduced water content, and increased calorific value. • Potentially increased calorific value of char and gas as byproducts of co-pyrolysis.	• Feedstock is available worldwide. • The volume of waste can be significantly reduced as more waste is consumed as feedstock. • The cost of waste treatment is saved. • Environmental problems are solved. • No waste is produced by the process. • The process can be easily applied to existing plants for biomass pyrolysis.

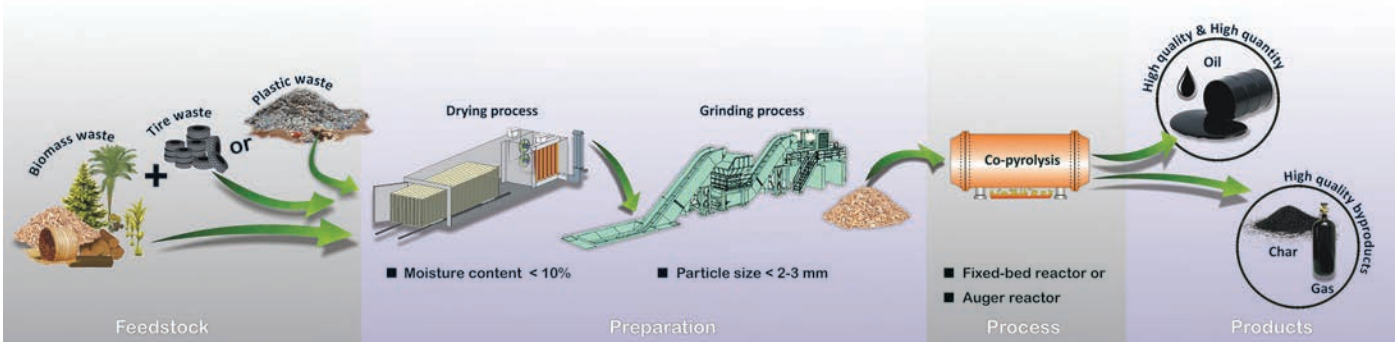
research has shown that both the quality and quantity of oil are improved when co-pyrolysis is used. The additional yields of liquid products that can be obtained through this process vary in the range of 2–23 wt%. The detailed features of co-pyrolysis are summarized in Table 1.

Co-pyrolysis is performed in a reactor system (generally a fixed-bed or auger type) with moderate operating temperatures and in the absence of oxygen. Oil production involves three basic steps: preparation of samples, co-pyrolysis, and condensation (Fig. 1). Prior to pyrolysis, the biomass sample should be prepared to have a moisture content lower than 10% and biomass particle sizes smaller than 2–3 mm. The low moisture content will prevent water content in the oil, and small biomass particle sizes achieve high biomass heating rates. The temperature process can be adjusted within the range of 400–600°C to maximize the production of oil (more than 45 wt% of oil can be produced). The temperature of the vapor produced in the pyrolysis unit must be maintained at >400°C before reaching the condensation unit. It is important to minimize liquid deposition, and blockage of the equipment and piping system should be avoided.

While the main benefit of using co-pyrolysis method is a significant reduction in the volume of waste due to more waste being consumed as feedstock, co-pyrolysis offers the added benefits of reducing landfill space, waste treatment costs, and environmental impacts. Since landfill disposal is undesirable, this method could be proposed as an alternative waste-management procedure for the future that will have a significant impact on waste reduction and could also enhance energy security. From an economic point of view, co-pyrolysis has been found to be a promising option for converting biomass into pyrolysis oil. The authors note that the use of co-pyrolysis techniques is more profitable than pyrolysis of biomass alone, and that co-pyrolysis also has potential for commercial development. They also identified the tipping fees obtained for the raw materials used in the process as the key to overall profitability.

The liquid fuel from biomass, especially wood-based biomass, has a lower energy content than fossil fuels. However, the energy content can be significantly improved by adding other types of waste material, such as tire and plastic. The use of tire waste as a co-feed has proven to increase oil yields, and research has shown that increasing the percentage of tire mass during the pyrolysis of wood biomass increases the calorific value of the oil. Unfortunately, tire waste can also increase the sulfur content in the oil, which must subsequently be desulfurized before it can be used for combustion. (Oxidative desulphurization is an effective technique.)

FIG. 1. Co-pyrolysis of biomass



Because plastic waste is made from crude oil, it can make a positive contribution to energy content. Generally, the liquid product from pyrolysis of plastic alone has a competitive calorific value compared to wood biomass. Indeed, values of more than 40 MJ/kg have been obtained.

It should be noted that not all types of plastic are recommended for pyrolysis. Unlike other commercial plastics, polyethylene terephthalate (PET) and polyvinyl chloride (PVC) are not preferred since they produce very low liquid oil yields of between 10–25 wt%. The benzoic acid in PET and the chlorinated compound in PVC also depreciate fuel quality, resulting in calorific values that are below 30 MJ/kg. Even if these shortcomings could be overcome, PET is also not an economical feed option, because the benzoic acid content in PET pyrolysis oil is a general sublime that can clog piping and heat exchangers, and hydrogen chloride (HCl) released from PVC pyrolysis is so toxic and corrosive that it can damage processing equipment (Table 2).

The oil produced through pyrolysis using other commercial plastics (Fig. 2), such as high-density polyethylene (HDPE), low-density polyethylene (LDPE), polypropylene (PP) and polystyrene (PS), all have calorific values significantly above 40 MJ/kg—a value that is considered high for energy utilization. The amount of liquid oil produced is also high. PS produces the highest amount of liquid oil (up to 97wt%). LDPE produces the highest amount (93.1wt%) of liquid oil in the polyolefin plastic category, followed by HDPE (84.7wt%) and PP (82.12wt%), provided the thermal pyrolysis process is conducted at an effective temperature of 500–550°C. Higher temperatures favor the formation of gas products. In terms of oil appearance, wax formation starts to dominate the product in the pyrolysis of HDPE and LDPE plastics at the effective temperature mentioned previously. Wax formation in the oils from polyethylene-type plastics is caused by improper cracking of plastics to high molecular mass hydrocarbon components. The oils from other plastics remain liquid throughout the process.

TABLE 2. The use of plastic and tire wastes as a co-feed

Type of wastes	Description
Tire	• Increases the oil yield • Increases the calorific value of liquid product • Reduces the aqueous phase formation • Increases the sulfur content in liquid • Contributes to methane production • Not favorable for increasing the fuel characteristics of char • Helpful in reducing the reaction time to maximize the production of methane and hydrogen • Additional preparation may be needed to remove steel thread or textile netting from the tire.
Polyethylene terephthalate (PET)	• Not suitable for pyrolysis • Produces low liquid oil (20-40wt%) and high volatile product • Oil composition contains benzoic acid that can clog piping. • Oil has very low calorific value which is less than 30 MJ/kg.
High-density polyethylene (HDPE)	• Good for pyrolysis • Converts into the mixture of liquid and wax in thermal pyrolysis • Produces high oil/wax yield which is more than 80wt% • Oil/wax has high calorific value above 40 MJ/kg.
Polyvinyl chloride (PVC)	• Not suitable for pyrolysis • Oil composition contains hydrogen chloride (HCl) that can damage process equipment when heated moderately. • Produces very low liquid oil less than 15wt% and high volatile product • High tar accumulation • Oil has the lowest calorific value which is less than 30 MJ/kg.
Low-density polyethylene (LDPE)	• Good for pyrolysis • Converts into the mixture of liquid and wax in thermal pyrolysis • Produces high oil/wax yield which is more than 80wt% • Oil/wax produced has high calorific value (~ 40 MJ/kg).
Polypropylene (PP)	• Good for pyrolysis • Produces high liquid oil yield more than 80wt% • Has lower starting degradation temperature than HDPE • Oil has high calorific value above 40 MJ/kg.
Polystyrene (PS)	• Very good for pyrolysis • Produces the highest liquid oil production more than 90wt% • Starts to degrade at the lowest temperature of 350°C • Oil has the highest calorific value among all plastics (above 40 MJ/kg).

Fig. 2. Polystyrene and tire wastes are recommended to use as a co-feed in co-pyrolysis to produce liquid fuel

The physical properties of pyrolysis oil from plastics (except those from PET and PVC) are comparable to commercial gasoline and diesel in terms of viscosity, density, very minimal ash content, and high calorific value. With respect to chemical properties, the pyrolysis oil from plastics has a greater aromatics content relative to its paraffin content. This explains the lower pour point, aniline point, flash point, and diesel index of the oil product compared to commercial gasoline and diesel. Nevertheless, the ignition quality of the fuel oil can be improved by mixing with additives, a method is growing in acceptance. Additionally, the low sulfur content in the pyrolysis oil obtained from plastics makes such oil suitable for use as fuel as well as cleaner for the environment.

Wastes of plastics and tires not only have a high energy content, but are also particularly easy to find and available in huge amounts in countries around the world. On the other hand, the sources of wood biomass that can be utilized for alternative energy vary significantly from country to country. Pyrolysis of the blends of those materials with other biomass wastes will encourage the creation of innovative new concepts in waste management, energy security enhancement, and environmental sustainability. Therefore, the development of the co-pyrolysis process to produce liquid fuel may be applicable in most countries.

Faisal Abnisa is a Doctor in Chemical Engineering from the University of Malaya, Malaysia. He has been actively involved in the research of pyrolysis of biomass since 2008, and has published extensively. Currently, he is working as a postdoctoral research fellow in the Department of Chemical Engineering, University of Malaya. His research interests focus on the thermal conversion of biomass and the use of pyrolysis liquid for fuel and chemical products. He can be contacted at faisal.abnisa@gmail.com.

Shafferina Dayana obtained her bachelor degree in Chemical Engineering from McMaster University, Canada, with a specialization in polymers. Currently, she is actively involved in the research of plastic pyrolysis at the University of Malaya.

Professor Wan Mohd Ashri Wan Daud received his PhD degree in Chemical Engineering from the University of Sheffield in 1996. After nine years as an academic and scientist at the Faculty of Engineering, he became Professor of Chemical Engineering in 2005. Since then, he has worked as a professor of chemical engineering at the University of Malaya, Malaysia. His research fields include energy, biomass conversion to bio-fuel, catalysts synthesis, polymerization and separation processes, and hydrogen storage.

Further reading

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Notice of Annual Business Meeting

AOCS' annual business meeting will be held on Monday, May 1, 2017 at 10:30 am at the Rosen Shingle Creek Hotel, Orlando, Florida, USA. Routine business of the Society will be conducted.

Held in conjunction with the

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Fundamentals of Edible Oil Processing

Organizer: Sefa Koseoglu, Filtration and Membrane World LLC, USA
Saturday, April 29

Knowledgeable speakers from industry and academia will discuss unit operations, processing conditions and their effect on minor compounds, chemistry, texture, crystallization and nutritional quality of final product.

Designed for:

- Recent graduates and newcomers to oils and fats industry
- Processors
- Product Formulators
- Chemists and Technicians
- Marketers and business managers who desire to be familiar with the edible oil processing industry

New Techniques in Edible Oil Processing and Refinery Optimization

Organizer: Sefa Koseoglu, Filtration and Membrane World LLC, USA
Sunday, April 30

Meet experts in the field, discuss their current challenges, and enhance your product innovation and plant operation. Energy savings and waste water reduction in oils and fats will be discussed, as well as learning to increase productivity as it relates to soybean, sunflower, corn, palm, and other tropical oils.

Designed for:

- Product Technicians
- R&D Engineers
- Engineering Supervisors
- QA Technicians
- Project Engineers
- Process Improvement Engineers
- Business Development Managers
- Sales and Marketing Specialists
- Equipment Manufacturers
- Product Formulators
- Plant Engineers
- Processors
- Chemists
- Technicians

Experimental Design and Analysis: Simple Tools to Maximize Product Performance

Organizer: Arun Ramchandran, University of Toronto, Canada
In cooperation with the AOCS Surfactants and Detergents Division
Sunday, April 30

Learn the concept of Experimental Design as it applies to formulation and mixture design, maximizing efficiency with experiments, and using statistical tools to validate results.

Designed for:

- R&D Chemists and Engineers
- R&D Technicians
- Technology Managers
- QA Technicians
- Project Engineers
- Business Development Managers
- Product Formulators
- Plant Engineers
- Processors
- Chemists
- Technicians

Is there a realistic solution to upgrading bio-oil to fuels and chemicals?

Ahmed Halilu

- Converting bio-oil to fuels and platform chemicals offers considerable advantages.
- In spite of proliferating research, the lack of an integrated process for optimizing the production of such valuable products within a single bio-refinery facility could limit their application.
- An applications approach that includes industry support for bio-oil upgrading studies and scale-up work could help fill the gap.
- This article proposes a framework for research that could lead to the realistic production of platform chemicals and fuels products from bio-oil for practical applications.

Crucial attempts to convert lignocellulose biomass to bio-oil have been made [1–5]. Most bio-industries are unwilling to invest in such efforts without validation of bio-oil's practical relevance on an industrial scale.

Similarly, while there are considerable advantages to converting bio-oil to automobile-grade fuel; C_6-C_{14} or jet fuels hydrocarbons; C_8-C_{22}; as well as C_6 categories of platform chemicals [6], the lack of an integrated process for optimizing the production of such compounds within a single facility could limit their application as promising fossil supplants.

Given that the straight-on production and practical application of bio-oil based products hinge on addressing such concerns, it is ironic that most research proliferations on biomass conversion to fuels and chemicals do not tackle this problem. Indeed, a review of indexed literature in web of science revealed that ~ 63.4 % of the research is conducted on a laboratory scale, while only about ~ 36.6 % of the research focuses on applications at an industrial level.

STABILIZATION/TRANSFORMATION OF BIO-OIL COMPOSITION DIVERSITIES

Bio-oil originates from thermochemical, biochemical, or chemical conversion of lignocellulose biomass into more than 300 oxy-functionalized molecules [3, 7]. The effect of these molecules co-existing in multiphases contributes to the high viscous nature of bio-oil. This report emphasizes hydrothermal liquefaction (HTL)—N_2 or H_2O reaction environment, 280–450 °C, 30 bars and ~5-30 min—and pyrolysis. These are two thermochemical routes robust in converting broad ranges of lignocellulose sources, such as wood biomass and non-woody biomass (Fig. 1, L1). HTL-derived bio-oil has typical compositions: carbon (68–81 wt. %); sulphur and nitrogen (0.1 wt. %); oxygen (9–25 wt. %); water (6–25 wt. %); and density (1.10–1.14 wt. %) [8-11]. Complimentarily, pyrolysis-derived bio-oil also has typical compositions: carbon (56–66 wt. %); sulphur and nitrogen (0.1 wt. %); oxygen (27–38 wt. %); water (24–52 wt. %); and density (1.10–1.2 wt. %) [1, 8].

The optimal potency of bio-oil from either of these methods for fuels or chemicals entails stabilization/transformation of the composition diversities. Most bio-oil improvement techniques have consolidated tendencies to selectively consume targeted $C(sp^2)$-O, $C(sp^3)$-O or

C-C-based functionalities. Other plausible approaches include lignocellulose biomass conversion to nano cellulose, then ethanol and glucose (Fig. 1, L2), or gasification to fuel and chemicals (Fig. 1, L3). As shown in Fig 1, T1, bio-oil fluidity, in addition to affecting supplementary performance properties for fuel, is usually restored via catalytic hydroprocessing upgrading techniques.

Upgrading techniques such as emulsification, one-step hydrogenation-esterification, acetylation, and ketonization center on consumption of bio-oil aldehyde-organic acids functionalities for the chemistry of C-C formation. These eliminate bio-oil chemical instability, aging, and high acidity issues. In contrast, vapor phase hydrogenation, hydro-deoxygenation, catalytic cracking, and steam reforming processing techniques also focus on the chemistry of C-O cleavage, C-C bond formation, and other bio-oil functionalities such as those shown in Fig. 2, A, and Fig. 2, B (page 24). Consequently, it seems obvious that targeting bio-oil oxy-functionalities should be the focus of research on bio-oil upgrades. Yet, most of the research does not focus on industrial-scale scenarios. Other issues include product and catalyst separation, challenges in the design of a suitable catalytic environment, and setting up of an economically feasible process. These challenges inclusively suggest catalyst-activity and catalyst-design serendipity as an imminent research focus that could spur industry involvement.

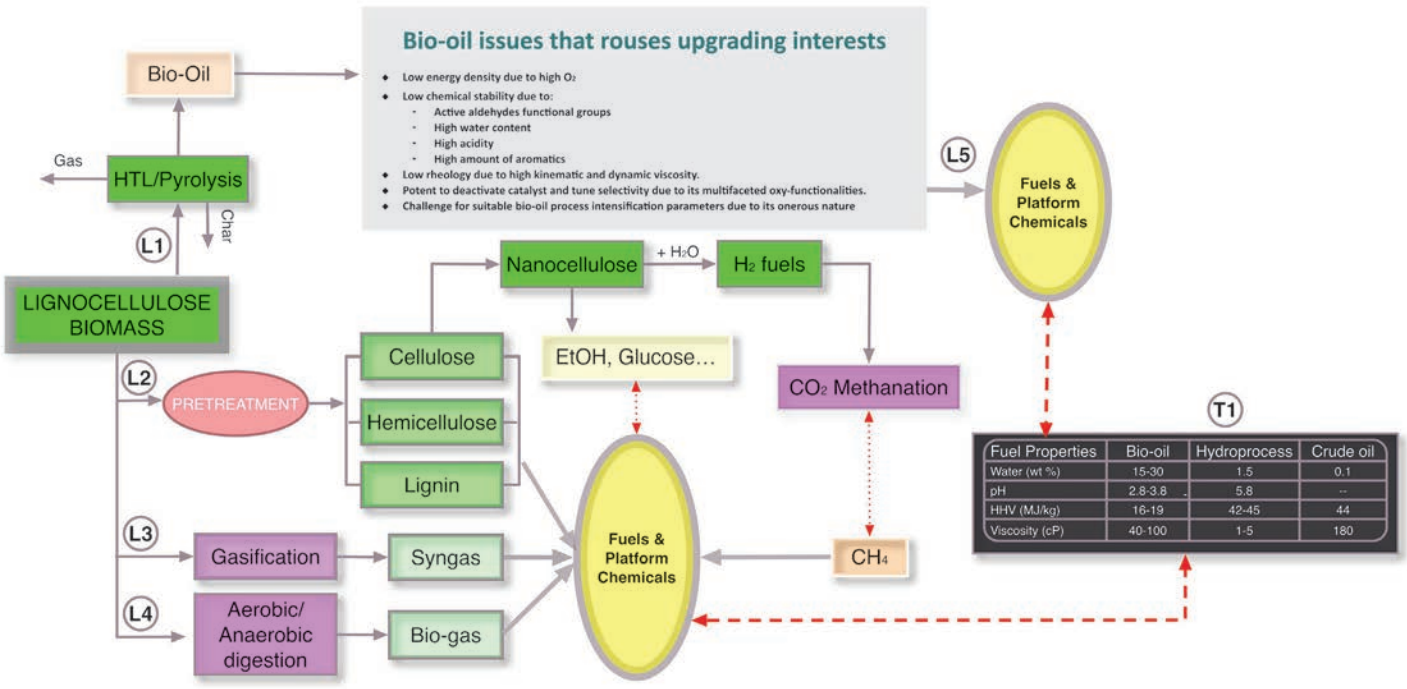
EVALUATING UPGRADED BIO-OILS FOR FUEL AND CHEMICAL APPLICATIONS

Evaluating upgraded bio-oil should commence with the following requisite approaches:

- proof of concepts experiments using model bio-oil compounds for data acquisition purposes. These model compounds are representative molecules with functionalities that corroborate real bio-oil, and
- real bio-oil feedstock for the production of chemicals and fuel through hydroprocessing techniques.

It is important to note that the upgraded bio-oil for fuel applications is valued based on its energy content. The efficiency of the upgrading process offers a high energy density (MJ/L) that is independent of composition diversity. In essence, high energy in mega joules can be obtained from a very small metric measurement in liters or kilograms. For instance, bio-oil has a low energy density of 16–19MJ/Kg, so the target is to achieve a high energy density (~34.8MJ/L) typical of aviation fuel or jet fuel [4, 12–14]. These energy measurements in units of MJ/L are the gravimetric energy, which is high due to increasing energy density from reducing oxygen through C-O bond cleav-

FIG.1. Lignocellulose biomass conversion opportunities for compositional diversity



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ages during hydroprocessing. This is complimented by regulating the weight of the fuel through C-C formation.

Fluidity is another parameter for evaluating upgraded bio-oil for fuel applications. Upgraded bio-oil should offer a low-pressure drop profile during practical applications. And, although the anti-knocking property of a fuel depends on its aromatic content, the aromatics of upgraded bio-oil should be low at a level that agrees with the 95–97 values of octane numbers [15, 16]. Bio-oils lower in aromatics will produce less combustion smoke than benzene and its derivative. Other performance properties worthy of evaluation include storage and thermal stability, volatility, and non-corrosiveness. Finally, the upgraded bio-oil should exhibit slow solidification and at the same time contribute to a good combustion and ignition profile for fuel applications.

Expanding further, upgrading bio-oil for chemical use involves products that can be used directly as high-purity chemicals. These include hydroxymethylfurfural, furfuryl alcohol, benzene, phenol, sorbitol, and anisole guaiacol, among others (Fig 2). Although it would be impossible to mention all of the chemicals that could be derived from upgraded bio-oil, upstream sep-

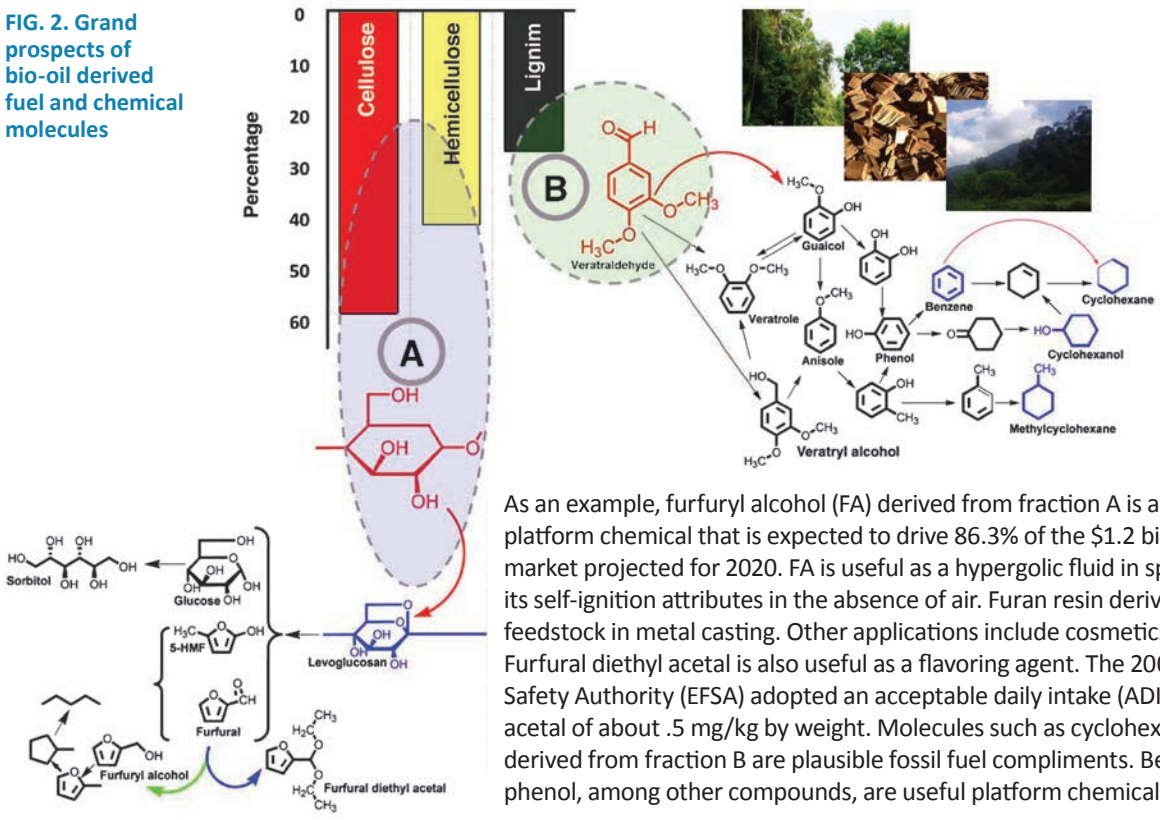

FIG. 2. Grand prospects of bio-oil derived fuel and chemical molecules

As an example, furfuryl alcohol (FA) derived from fraction A is a potent fuel and platform chemical that is expected to drive 86.3% of the $1.2 billion total furfural market projected for 2020. FA is useful as a hypergolic fluid in space rocket fuel due to its self-ignition attributes in the absence of air. Furan resin derived from FA is a useful feedstock in metal casting. Other applications include cosmetics and pharmaceuticals. Furfural diethyl acetal is also useful as a flavoring agent. The 2004 European Food Safety Authority (EFSA) adopted an acceptable daily intake (ADI) for furfural diethyl acetal of about .5 mg/kg by weight. Molecules such as cyclohexane and cyclohexanol derived from fraction B are plausible fossil fuel compliments. Benzene, gualacol, and phenol, among other compounds, are useful platform chemicals for chemical synthesis.

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aration and product purification are key items to be considered when upgrading bio-oil for chemical applications.

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The author acknowledges the National Research Institute for Chemical Technology, NARICT Nigeria.

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Home ozone processing: protecting healthful lipids in seafood

Charles Odilichukwu R. Okpala

Fish and fishery products are a major dietary source of healthful long-chain polyunsaturated fatty acids (PUFA), particularly the omega-3 fatty acids eicosapentaenoic acid (EPA) and docosaphexaenoic acid (DHA). Unfortunately, these healthful omega-3 fatty acids have double bonds that facilitate a deteriorative process that causes lipid breakdown in seafood. This process proceeds through a free radical chain mechanism, known as lipid oxidation, which includes three distinct stages: 1. initiation (abstraction of hydrogen radical {H*} to yield free lipid radical {R*}), 2. propagation (combination of oxygen with free lipid radicals to form peroxyl radicals {RO_2*} eventually to lipid hydroperoxides {RO_2H}), and 3. termination (subsequent reactions that lead to non-radical products) (Fig 1.).

- **Lipid oxidation damages healthful long-chain polyunsaturated fatty acids (PUFA) and is an important cause of deterioration in seafood.**
- **Evaluations of the levels of gases produced from seafood breakdown have shown that ozone treatment has the potential to extend the shelf life of fishery products.**
- **Recently, the ability of home ozone processing to reduce/slow down lipid damage during iced storage was evaluated using measurements that quantified primary and secondary lipid products.**

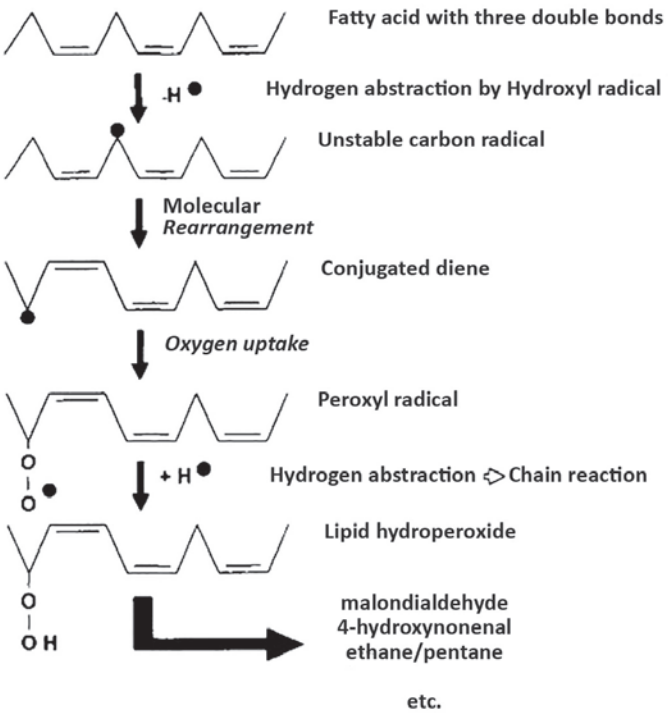
Both initial and propagation stages are also considered to result in different intermediate end products. Many published lipid oxidation studies largely focus on one single aspect of reaction, such as analyses of specific catalysts, antioxidant effects of oxidation, and kinetics of oxygen uptake [1]. So as hydroperoxides evolve during iced storage of post-harvest fishery products, kinetic curves can be elucidated by two stages involving induction and propagation (Fig 2). In addition, the induction period (IP) has been defined as the point where peroxide value (PV) showed a sudden rise during iced storage (of ozone-processed shrimp). Clearly, it can be seen that the intersection points of two linear regression lines define the end of IP in terms of time. Hence, better knowledge and understanding of lipid oxidation mechanisms, especially the formation of hydroperoxides, is critical to developing more effective control measures in bio-food systems [3–4].

OZONE IN FOOD PROCESSING

Ozone (O_3) is a bio-based, environmentally friendly, broad-spectrum antimicrobial that kills a wide variety of bacteria, viruses, and fungi. Ozone's use in food processing has become increasingly widespread since 2001, when the US Food Drug Administration (FDA) amended US food additive regulations to provide for the safe use of ozone in gaseous and aqueous phases as an antimicrobial agent on food, including meat and poultry [5].

Ozone discharge, whether in aqueous or gaseous phase, must adhere to current standards of good manufacturing practice. When used directly on food, two additional factors must be taken into consideration: 1. the minimum exposure to ozone that is required to provide anti-microbial benefits to specific foodstuffs, and 2. the threshold at which ozone damages food within permissible exposure levels/environmental limits set by the US Occupational Safety and Health Administration (OSHA) and the US Environmental Protection Agency (EPA). These levels can only be

FIG. 1. Basic reaction sequence of lipid peroxidation. Republished with permission from *Biochem. Soc. Trans. 29*: 358–362, 2001



determined from experimental investigations. Nevertheless, because ozone requires no storage or special handling/mixing considerations, it still offers several advantages over other chemical sanitizers used in the food industry [5, 10]. Some advantages of ozone treatment over other non-thermal food processes are shown in Table 1.

In the seafood industry, ozone is used to reduce pathogens in hatcheries and growing ponds, to sanitize processing equipment and surfaces, and to extend shelf life. More recently, ozone use has evolved to include household ozone-generating devices that purify tap water, clean laundry, remove odors, and clean fruits and vegetables. This form of ozone technology also shows promise as an additional point of intervention in the food industry [1–3].

CAN HOME OZONE TREATMENT PREVENT LIPID DAMAGE IN CRUSTACEANS?

The author recently used a household ozone-generating device (the O_3 Fresh™, Model SQ8-BA, Ovoproducts, Leicestershire, UK) to study ozone-processed shrimp during iced storage. The O_3 Fresh device complies with the European Council Directive 73/23/EEC and 93/68/EEC (as amended), and is typically used in home kitchens to disinfect fruits and vegetables. Operated at ~ 25°C, it has a built-in ozone concentration discharge of 100 mg/h into water, a wash and spin capacity of 4L, and three exposure levels/wash cycles of 1, 3, and 5 minutes: all of which were fixed by the manufacturer. As with other home-use models, ozone treatment levels can be adjusted by varying the ozone exposure/wash cycle times. The device contains an evenly perforated, removable basket that conveniently accommodates fresh food item(s). When the wash cycle knob is switched "on," the removable basked spins in sinc with the ozone discharge to allow for rapid and regular, yet even distribution of ozone constituent particles within a (recommended tap) water medium. When the wash cycle is completed, the water automatically drains off safely [2–3, 7–9].

The effects of minimal/lowest exposure levels (compared to control/untreated) were studied first, before increasing ozone discharge levels. Lipid degradation was assessed using lipid damage parameters such as peroxide value (PV), *para*-anisidine (*p*-AnV), and 2-thiobarbituric acid reactive substances

FIG. 2. The induction period (IP) for the formation of hydroperoxides as shown by the measured mean values for peroxide values (PV).The intersection of two linear regression lines generates the point to indicate the end of the IP (PV_{IP}). Using the slopes of fitted regression lines, the respective oxidation rate constants k_1 and k_2 for induction and propagation can be determined. Republished with permission from *Food Biosci. 16*: 5–10, 2016

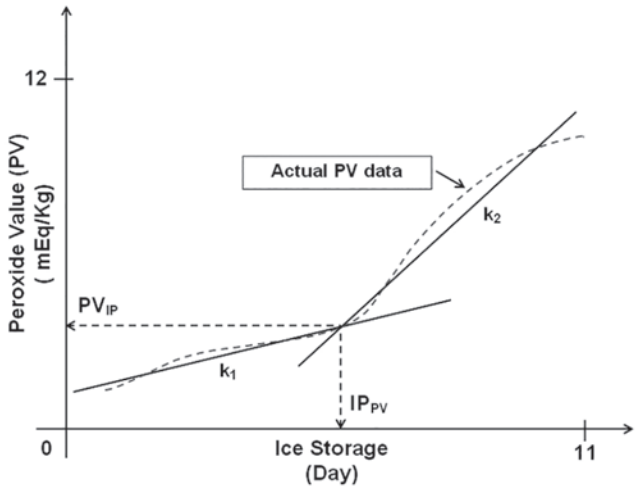


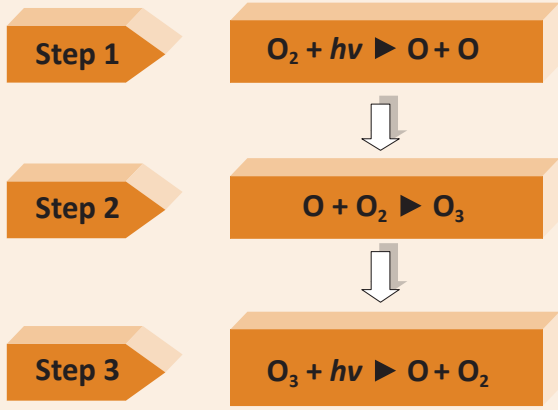
TABLE 1. Some benefits of ozone treatment compared to other non-thermal food process techniques

Ozone Treatment	High Pressure Treatment (HPT)	Modified Atmosphere Packaging (MAP)
Very high sanitizing capacity	Moderate/high sanitizing capacity	Moderate sanitizing capacity
Generally Recognized As Safe (GRAS) status	Not yet with GRAS status	Not yet with GRAS status
Household device commercially available	No household device commercially available	No household device commercially available
Very high potential application for seafood products	Limited potential application for seafood products	Relatively high potential application for seafood products

Ozone formation

As a highly unstable triatomic oxygen molecule, ozone can be discharged in commercial quantities, especially when oxygen molecules are subject to high-voltage electric discharge. It is the splitting of molecular oxygen into two atoms that brings about highly reactive moieties, some of which can combine to form ozone, as showed in the schematic. For oxidation purposes, the rapid degradation of ozone to molecular oxygen releases a free oxygen atom that either reacts with another oxygen atom to form an oxygen molecule or combines with other chemical moieties [3].

Oxygen splitting to form ozone



(TBARS). Specifically, PV was used to quantify the primary lipid oxidation products, such as hydroperoxides, whereas *p*-AnV was used to quantify the secondary lipid oxidation products associated non-volatiles, such as 2-alkenals and 2,4-alkadienals. Furthermore, TBARS were used to quantify other secondary lipid oxidation products such as malonaldehydes (MDA), the latter being among key products of PUFA degradation.

Interestingly, the results showed that the ozone treatment had a significant effect on lipid damage products [2–3, 7–9]. The progression of lipid oxidation parameters of ozone-processed (OP) and control/untreated shrimp during iced storage is schematically depicted in Fig. 3.

Ozone treatment was also found to somewhat delay the sudden rise in PV, *p*-AnV, and TBARS, and these parameters appeared less progressive in the OP shrimp compared to control samples. Regardless of ozone treatments, *p*-AnV and TBARS seemed to increase at a much faster rate compared to PV, probably due to PUFA that generated secondary oxidation products well before propagation phases [1]. Kinetic studies of the effects of increasing ozone exposures in OP shrimp showed that both induction period (IP) and PV at induction period (PV_{IP}) during iced storage were lower in samples of the OP shrimp than the control shrimp [3]. That less lipid damage occurred in the OP samples strongly suggests that ozone safely

Information

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discharged using a household device can help preserve the lipids in shrimp during iced storage.

Overall, the large amounts of PUFA moieties in shrimp are believed to increase their vulnerability to lipid autoxidation. Considering previously published literature in this area, these first-reported findings specific to the effects of household ozone treatment on the lipids in shrimp suggest that the potential of household treatment has not been fully explored. Thus, more robust lipid-related data could help to further validate not only the capacity of ozone treatment as a safe technology but also as a way for consumers to maximize the health benefits they get from the seafood they eat.

Charles Odilichukwu R. Okpala earned a Master of Research in Food Science from the University of Strathclyde in Glasgow, UK. He recently completed a research fellowship at the Istituto per l'Ambiente Marino Costiero—Consiglio Nazionale delle Ricerche (IAMC-CNR) in Mazara del Vallo, Italy. He has more than 20 published articles in peer-referred journals, and devotes the majority of his research to food processing and quality, and innovative food technology applications. He can be contacted at charlesokpala@gmail.com.

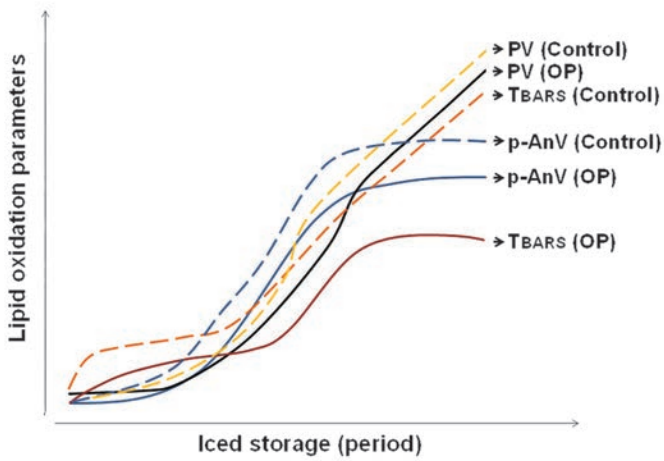

FIG. 3. Schematic representation of evolution of lipid oxidation (PV, peroxide value; p-AnV, para-anisidine value; and TBARS, 2-thiobarbituric acid reactive substances) parameters of ozone-processed (OP) and control (untreated) shrimp during iced storage. Republished with permission from *Lipid Technol. 28*:93–95, 2016

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JSD CELEBRATES 20TH VOLUME WITH 5 SELECTED ARTICLES

Five articles have been selected in recognition of the *Journal of Surfactants and Detergents*' 20th anniversary year. The articles were chosen because they were either highly-cited, most-downloaded, of general significance, or cover investigations important to surfactants and detergents researchers. Here, two of the articles are summarized by *JSD*'s Editor-in-Chief, George A. Smith. Summaries of the other three articles will appear in future issues of *Inform* throughout 2017. Full versions of all five articles are available at www.springer.com/jsd.

NEW ANIONIC ALKYLARYL SURFACTANTS BASED ON OLEFIN SULFONIC ACIDS

Paul D. Berger and Christie H. Lee
JSD 5: 39–43, 2002, http://link.springer.com/article/10.1007/s11743-002-0203-3.

Linear alkybenzene sulfonate (LAS) has been the work horse anionic surfactant for powder detergents for many years. The main limitations of LAS are limited solubility in water and poor hard water tolerance. To overcome these limitations, Berger *et. al.* has developed a process to produce a new family of anionic surfactants by air/SO3 sulfonation of olefins followed by alkylation of aromatic compounds using the olefin sulfonic acids. The new products have a sulfonate group attached to the alkyl chain rather than the aromatic group. Mono- and disulfonated surfactants as well as gemini type surfactants can be prepared. In general, the new anionic surfactants show improved water solubility over conventional LAS.

ENHANCING SOLUBILIZATION IN MICROEMULSIONS—STATE OF THE ART AND CURRENT TRENDS

Jean-Lois Salager, Raquel E. Antón, David A. Sabatini, Jeffrey H. Harwell, Edgar J. Acosta, and Laura I. Tolosa
JSD 8: 3–21, 2005, http://link.springer.com/article/10.1007/s11743-005-0328-4.

Many applications require solubilization of large amounts of insoluble material. Maximum solubilization occurs in Winsor III microemulsion systems when a bicontineous microemulsion is in equilibrium with excess oil and water. Increasing the size of the surfactant will increase the interaction with the oil and water phase and increase solubilization but this approach is limited by solubility constraints. Solubilization enhancement can be accomplished using hydrophilic or lipophilic linking groups which modify the structure of the water or oil phases close to the interface. Covalently bonding the hydrophilic and lipophilic linking groups together results in an extended chain surfactant which can enhance solubilization without selective portioning in the water or oil phases. Enhanced solubilization requires a smooth transition in hydrophilicity across the structured interfacial region.

Structuring with peptides

Advanced Materials is a regular column featuring novel materials of interest to the oils and fats community.

Fiona Case

Among the biomolecules, proteins and peptides (short proteins) are surely the masters of self-assembly. While the DNA double helix is iconic; and RNA the poster-child for pattern recognition; the sheer number and diversity of protein and peptide assemblies is unprecedented. Little wonder then that materials scientists, have sought to capture and direct the self-assembly of peptides to create complex materials from simple building blocks.

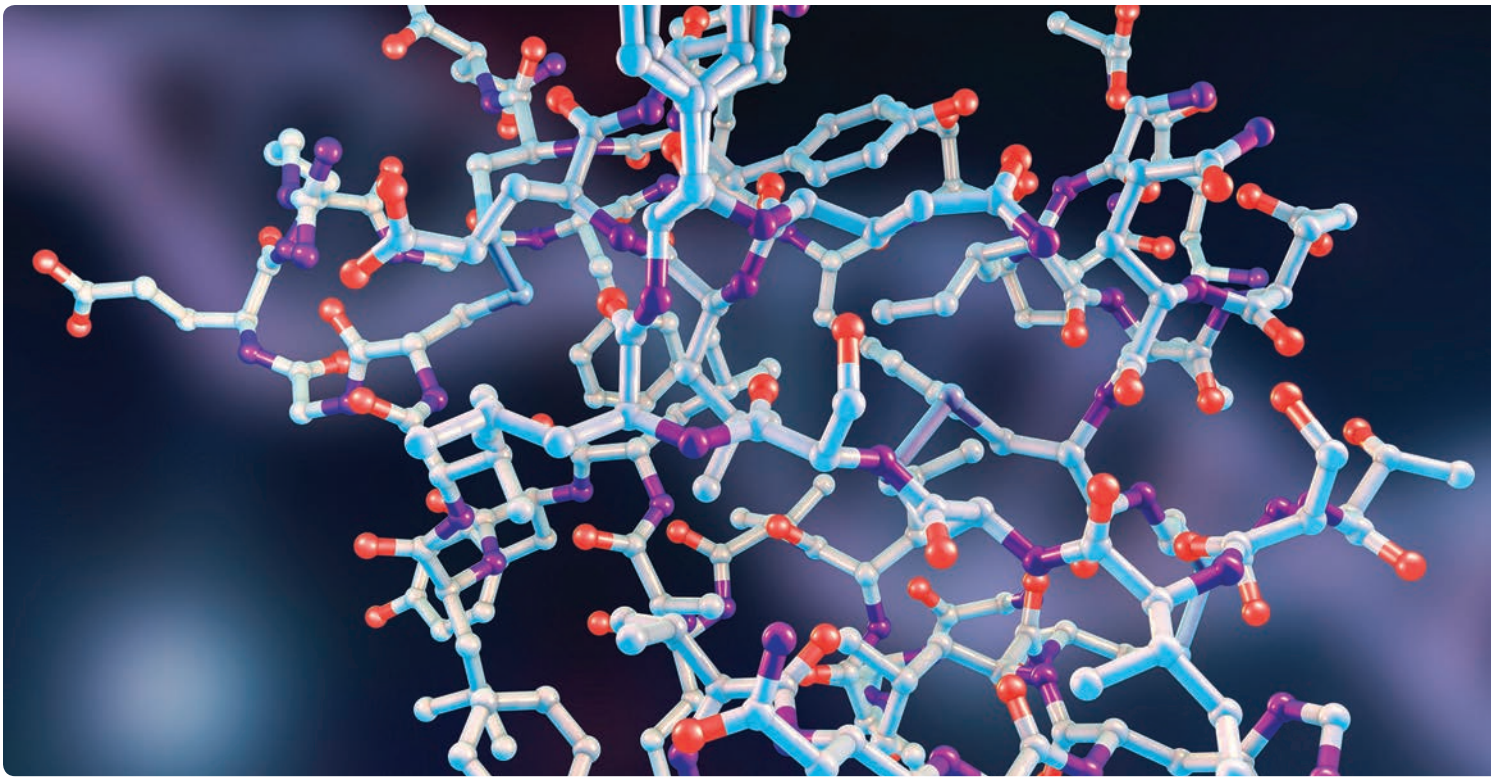
- **Peptides—short proteins containing as few as two or three amino acids—can self-assemble and create structure in water.**
- **Some structures create gels that are stable, but can be broken down by shear forces or changes in environment; others create fibrils that that wrap around and emulsify oil droplets.**
- **Such structures have interesting potential for foods and HPC (home and personal care) products, but identifying the optimum sequence of amino acids for a specific application is challenging due to the vast number of possible arrangements for 21 amino acids in even a short peptide chain.**
- **Optimization strategies involving computational chemistry, dynamic combinatorial libraries and high-throughput technologies have been proposed, and are described in this article.**

In 2003, Ehud Gazit, a professor of molecular microbiology and biotechnology at Tel Aviv University in Israel, discovered the self-assembly of di-phenylalanine (FF), and observed that short aromatic peptides (pentapeptide and shorter) could form well-ordered amyloid fibrils—research that has led to new insights into diseases such as Alzheimer's. Gazit has proposed that these structures be used as scaffolds for nanoelectronics applications and sensors.

Sequences inspired by naturally assembling systems, such as the prion proteins, have been extensively studied for biomedical applications. Researchers such as Shuguang Zhang, a professor in the Center for Biomedical Engineering at MIT in Cambridge, Massachusetts, USA, and Darrin Pochan, a professor of Materials Science & Engineering at the University of Delaware, USA, have identified sequences of amino acids which show potential as supports for biological tissue repair. Pochan's proposed sequences of 20 amino acid peptides containing valine and lysine repeats self-assemble to form a gel which can shear thin as it is injected and then quickly restructure once in the body.

In 2006, Annette F. Dexter and Anton Middelberg created a startup company, Pepfactants Pty Ltd, at the University of Queensland in Australia, which promoted a 21-residue peptide as a stimuli-responsive surfactant that switches molecular architectures at a fluid–fluid interface in response to changes in bulk aqueous solution composition.

"This is indeed a very exciting field. Peptide assemblies may provide a very interesting use in industry," says Gazit. "It is clear that very short peptides—as short as dipeptides—can form functional assemblies. The physical properties are quite astonishing. The building blocks are simple, inexpensive, environmentally-friendly. Nature has used self-assembly to form various functional structures while avoiding the use of heavy and toxic metals as with inorganic materials."



The ability to create structure—particularly in water—is of great relevance in the foods and HPC (home and personal care) industries. The possible replacement of polymer structuring agents such as the carbopols with short peptides that can self-assemble, or disassemble, depending on their environment, offers the prospect of switchable rheology. There is the potential for other benefits too: If the peptide has surfactant properties, it could contribute to cleaning. Some peptides can replenish and rejuvenate skin: Surfactants with short peptide head groups, such as palmitoyl pentapeptides or palmitoyl tetrapeptides, are already used in moisturizers with anti-wrinkle claims. Peptides also offer excellent biodegradability and sustainability, valuable green credentials, and the potential for bio-based production.

The selection of a suitable self-assembling peptide is, however, challenging. Most of the systems studied thus far have been discovered by serendipity or are fragments of naturally occurring proteins, and many are dominated by hydrophobic amino acids which limits their application in water-based products. Among the vast number of possible sequences—there are 8,000 ways to arrange the 20 canonical amino acids in a tripeptide, for a 5 amino acid structure there are more than 3.2 million sequences, to store a milligram of each of the 20 amino acid peptides we should be prepared to set aside a space the size of Australia and 8.5 miles deep—there may be an optimum structuring agent for a specific application, but how to find that needle in that haystack?

SELECTING IN-SILICO

Computational chemistry provides an approach for identifying promising candidates among the shortest peptides, and providing guidance for selection of larger systems. Tell Tuttle, a senior lecturer at the University of Strathclyde in Scotland, is using simulation to predict the self-assembly behavior of libraries of peptides with specific focus on materials relevant to the foods and HPC industries. His in-silico screening identified the first unsubstituted tripeptides capable of forming hydrogels in water in the absence of organic solvents (the self-assembly peptide-based surfactants with alkane tails or peptides attached to large hydrophobic groups is well known).

The starting points for Tuttle's simulations are models of each peptide completely dispersed in water. As the simulations progress many of the peptides are predicted to be water soluble (they remain well dispersed). Others quickly aggregate, phase separating into an amorphous lump. However, a small number of amino-acid sequences show more interesting behavior: These are peptides including hydrophilic amino acids which are predicted to self-assemble in water to form stable structures. From an initial screening of all 8,000 tripeptides, Tuttle identified five worthy of further study. Further simulation of up to 9.6 μs (which is a long simulation for a molecular-scale model) predicted that three of these sequences (lysine-tyrosine-phenylalanine; lysine-phenylalanine-phenylalanine; and lysine-tyrosine-tryptophan) self-assembled to form fibers, and two others (containing diphenylalanine) formed bi-layer structures. Synthesis and characterization of these tripeptide solutions confirmed the computer-based predictions. Tuttle and his collaborator, Rein Ulijn, a professor and the director of the Nanoscience Initiative at the City University of New York, USA, synthesized the peptides and found that the three with preference for fibrillar assembly formed stable emulsions

with rapeseed oil. AFM showed the self-assembled fibrils wrapped around oil droplets.

"This is the first time emulsification has been seen for such short peptides," says Tuttle. "The modeling approach is particularly valuable because it reveals the mechanism of structure formation and insights into the driving forces for protein folding and self-assembly in these small systems"

Unsurprisingly, this work has attracted industrial interest. The bakery ingredient company Macphie of Glenbervie, Scotland, has been participating in the research.

"This is a very exciting project to be involved in," says Paul McKnight, a senior research and development manager at Macphie. "It has a tremendous bearing on what we do as a company due to the wide use of emulsifiers, stabilizers, and gellators across our product range, which includes sweet and savory sauces, dressings and batters required to make cakes and muffins."

EVOLVING EMULSIFIERS

Rein Ulijn has also developed a complimentary experimental approach using dynamic combinatorial libraries: The optimum sequence of amino acids for self-assembly in a specific environment is revealed over time as amino acids are permitted to exchange, and non-assembling peptides sequences are weeded out of the evolving system.

"We introduce an initial mixture of dipeptides to enzymes that can make and break bonds," explains Ulijn. "The enzymes aren't able to act on systems that are self-assembled into larger structures, so any amino acid sequence that is created which self-assembles will survive for longer, and become more prevalent in the mixture."

Many of the mixtures tested did not evolve into a unique stable structure, but some did. For example, when they started with a mixture of phenylanaline-serine (FS) and phenylanaline-aspartic acid (FD) dimers, the octamer FDFSFDFS was uniquely amplified. There was a transition from a transparent solution to a self-supporting hydrogel, and AFM and TEM images revealed the formation of an entangled fibrillar network. FDFSFDFS had been identified as a novel self-assembling peptide structuring agent.

One of the benefits of this approach is that the evolution can take place in the presence of co-solvents, salts, or small molecule structuring agents—a level of complexity that is not currently achievable in the modeling studies.

"For short peptides the process could be automated and expanded to include the entire peptide sequence space," says Ulijn, "allowing the optimum amino acid sequence and peptide length to be discovered for specific applications in the foods, cosmetics and personal care industry, and beyond."

ROBOTS TO THE RESCUE

Parallel synthesis and high-throughput testing may indeed be the ultimate solution for identifying materials for specific applications, using insights from modeling and from the initial experimental studies to reduce the huge combinatorial space. Automated parallel synthesis of short peptides is already well established in the pharmaceutical industry, where it is used to create focused libraries for testing as biologic drugs. The 8,000 possible tripeptides could be synthesized and purified in multi milligram quantities within 24 hours using high-throughput robotic machines. High-throughput testing techniques also exist. For example, dynamic light scattering (DLS) could provide an initial screen for sequences that form extended structure. A DLS plate reader can measure viscosity and monitor aggregation or self-assembly over sizes ranging from 0.5–1000 nm. Aggregation is detected as the self-assembled systems increase in size and hence diffuse more slowly in solution.

"Viscosity can be calculated by observing the motion of a polystyrene bead as it is buffeted around by the Brownian motion of the molecules in the solution: As the viscosity of the solution increases, the bead moves more slowly," explains Dan Some, a principal scientist at Wyatt Technology Corp. in Goleta, California, USA, manufacturer of such high-throughput DLS instruments.

Wyatt instruments can characterize 96, 384, or even 1,536 peptides without user intervention. The robotic system uses the same multi-well plates and liquid handling as the synthesis and purification systems.

"We haven't looked at peptide structure formation for food or personal care applications," says Some. "Our customers are typically studying peptides and antibodies as biologic drugs. Formulators are trying to avoid aggregation and gel formation since this can prevent injection of the drug or even produce an immune response."

But he sees no reason why the technique wouldn't work in the hunt for bio-based replacements for conventional structuring agents and emulsifiers.

"Automated DLS could provide either particle size distributions or viscosities on 96 peptide solutions within an hour," says Some. "All 8,000 tripeptides could be tested within a couple of weeks."

Insights and results from modeling studies and from directed evolution can help to focus the search by identifying which families of peptides are more likely (or unlikely) to create useful structures, and using robotic liquid handling equipment the addition of other ingredients—surfactants, salts—could also be automated, allowing the optimum peptide sequence for a specific product to be discovered.

"This is exciting," says Ulijn. "Our work, and the work of others, has demonstrated that there are short peptide sequences that form stable nanostructures, and are capable of structuring water, stabilizing emulsions, and acting as switchable rheology modifiers. The challenge is to identify the best sequences, within the vast combinatorial space available, for a specific application. Modelling, experimental approaches based on evolution of dynamic combinatorial libraries, and brute-force evaluation likely will all play a part in the search."

Advanced Materials is produced by Fiona Case, a freelance writer based in San Diego, California, USA. She can be reached at Fiona@casescientific.com.

Two new strategies to boost crop yields

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

Laura Cassiday

With a looming food crisis, devising new strategies to increase crop yields is now more important than ever. Experts predict that by 2050, the global demand for staple food crops such as corn, wheat, and soybeans will increase 70–100%. At the same time, the growing world population is making resources such as water and arable land increasingly scarce. The current annual increase in crop yields, around 1%, is insufficient to meet these demands.

Therefore, researchers are investigating new ways to make crop production more efficient. Two recent examples of this work, both from the lab of Dr. Stephen P. Long at the University of Illinois at Urbana-Champaign, demonstrate very different approaches to increasing crop yield. Used separately or in combination, these strategies could help meet the increased food demands of the future.

The first paper, published in *Global Change Biology*, describes a relatively low-tech method for increasing crop yield. By simply snipping off one-third of emerging soybean leaflets during the critical stage of seed filling, researchers increased seed yield by 8% (Srinivasan, S., *et al.*, http://dx.doi.org/10.1111/gcb.13526, 2016). This finding might be counterintuitive if one assumes that increasing leaf area should lead to higher rates of photosynthesis, and in turn, increased seed production. However, Srinivasan and colleagues used detailed mathematical models to predict that decreasing leaf area would actually increase seed yield, primarily because resources used to construct leaf tissue would be diverted to seed production. In addition, reducing leaf area was predicted to decrease water use by 11%.

In field trials, researchers removed seven emerging trifoliate leaves per soybean plant, corresponding to about 5% decreased leaf area. This treatment resulted in an 8% increase in seed yield. Although manually removing leaves from soybeans is not practical at a large scale, the researchers say that soybeans could be bred or genetically modified to produce fewer leaves. Srinivasan *et al.* estimate that an 8% yield increase across the United States would produce 6.5 million additional metric tons of soybeans annually.

The researchers concluded that modern soybeans produce more leaves than necessary, to the detriment of yield.

FIG. 1. Less is more. Researchers manually cut off new leaflets to decrease leaf area by just 5%, which increased yields by 8%.

Credit: University of Illinois

Elevated atmospheric carbon dioxide concentrations, as might occur under future conditions of climate change, are predicted to cause soybeans to produce even more leaves. Adding more leaves does not significantly increase photosynthesis because many of the additional leaves are shaded from sunlight by other leaves in the canopy. The wild ancestor of the soybean may have required more leaves to shade out competitor plants or compensate for leaf loss due to insects or disease, the researchers speculate.

The second paper by Long and his collaborators uses a more complex approach to enhance yield: By increasing the levels of three proteins involved in photosynthesis, the researchers boosted tobacco plant productivity by 14–20% (Kromdijk, J., *et al.*, http://dx.doi.org/10.1126/science.aai8878, 2016). To protect themselves from too much sunlight, plant leaves dissipate excess light energy as heat—a process called

nonphotochemical quenching (NPQ). When leaves become shaded by clouds or other leaves, the plants must shut down NPQ to avoid energy loss. However, this adjustment, or relaxation, is slow, and heat dissipation continues for many minutes after a leaf has been shaded. Using mathematical models to simulate the process on supercomputers, Long's lab calculated that this inefficient relaxation could reduce crop yields by up to 20%.

A caretonoid called zeaxanthin is important for NPQ. So the researchers boosted the expression of an enzyme called ZEP, which converts zeaxanthin to another molecule, violaxanthin, that does not promote NPQ. However, the team wanted to make sure that the plant could turn on NPQ quickly, if needed, so they also increased the expression of the enzyme VDE, which converts violaxanthin back to zeaxanthin. In this way, they hoped that NPQ could operate under conditions of full sunlight, but then quickly shut down when leaves become shaded. Kromdijk and colleagues also enhanced the expression of a third protein, PsbS, that increases the rates of both NPQ induction and relaxation.

In tobacco plants, these modifications resulted in faster NPQ relaxation and higher carbon dioxide uptake by leaves under fluctuating light conditions. When the plants were exposed to excessive light, NPQ was not compromised. In field trials, tobacco plants overexpressing the three proteins had 14–20% greater dry weight compared with wild-type plants.

"We don't know for certain this approach will work in other crops, but because we're targeting a universal process that is the same in all crops, we're pretty sure it will," said Stephen Long in a news release from the University of Illinois at Urbana-Champaign, dated November 17, 2016. The team is now working on repeating the work in various food crops.

"The United Nations predicts that by 2050 we're going to need to produce about 70 percent more food on the land we're currently using," Long said. "My attitude is that it is very important to have these new technologies on the shelf now because it can take 20 years before such inventions can reach farmers' fields. If we don't do it now, we won't have this solution when we need it."

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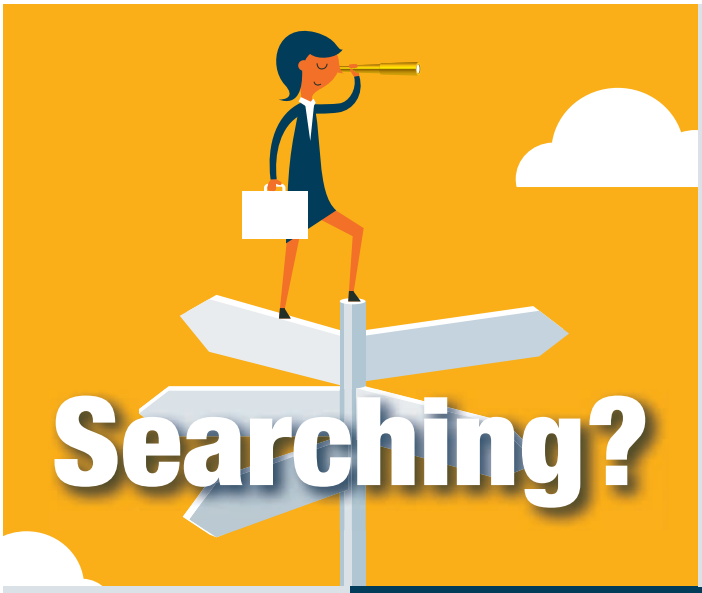
Olio is produced by Inform*'s associate editor, Laura Cassiday. She can be contacted at laura.cassiday@aocs.org.*



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New ACC center to assist with TSCA consortia

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

David Stegon

The American Chemistry Council (ACC) has created a new center to assist with the creation, support, and management of consortia around the implementation of the Lautenberg Chemical Safety Act (LCSA).

The Center for Chemical Safety Act Implementation will be managed by the ACC's Chemical Product and Technology Division. The center aims to be a resource for interested organizations to learn about the implementation of Toxic Substances Control Act (TSCA) reform—particularly with respect to use and exposure data, and testing requirements.

The center, which is open to both ACC members and non-members, will also serve as a starting point for affected manufacturers to collaborate on how best to meet future requirements.

"We wanted to create a one-stop shop that provided both ACC members and non-members with whatever they needed to navigate the new law," said David Fischer, ACC senior director.

"While the rule-making process is still going on, the ACC was very involved during the various aspects of the law's creation and have a good understanding of how the rules are intended to work."

While not an "apples to apples" comparison, Fischer said the ACC believes similar trends will emerge from LCSA implementation as did with REACH in the EU.

"With REACH, there were consortia that saw the benefit of working together with a shared interest and shared demands," Fischer said. "During REACH, we worked with a lot of groups and trade associations to learn how they helped members navigate the new regulations. We hopefully can bring some of those learnings into the center."

Along with facilitating consortia, the center has a number of stated goals to:

- manage generation of chemical information pursuant to the US EPA's new authorities under TSCA Section 4;
- develop chemical-specific use and exposure data;
- coordinate the review and comment on the EPA's draft chemical risk evaluations and proposed risk management actions; and

- engage with the EPA and other regulatory agencies, including the Office of Management and Budget (OMB).

Fischer said two areas of focus will be the implementation of sections 4 and 6 of TSCA.

Section 4 includes new testing requirements requiring manufacturers or processors to test chemical substances and mixtures.

Section 6 gives the EPA expanded authority to restrict existing chemicals that present unreasonable risk to human health or the environment.

"For Section 6, we want companies to be proactive and understand what they might want to focus on," regarding future substance restrictions, Fischer said.

"Based on what we know, manufacturers do not need to wait for specific [risk management] rules to be made before thinking about what changes will potentially come. We can help with that."

For further information about ACC's Center for Chemical Safety Act Implementation please contact David Fischer at david_fischer@americanchemistry.com or by phone at 202-249-6717 or Robert Simon at robert_simon@americanchemistry.com or 202-249-6700.

David Stegon is North America deputy editor of Chemical Watch.

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Flavor profile of meats: developing a lexicon and understanding flavor differences between grass- and grain-fed beef

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

Leslie Kleiner

Based on demand, consumers are starting to see more grass-fed beef at the supermarket, and with options come comparisons. To understand how to compare the sensorial properties of beef, as well as to learn how animal feed impacts flavor profile, I interviewed Professors Silvana Martini and Jerrad Legako, Department of Nutrition, Dietetics, and Food Sciences, Utah State University, Logan, Utah, USA.

Q: What are the current challenges in the sensory analyses of fresh meats, and how does the development of a lexicon for beef flavors aid in solving these challenges?

Current challenges in the sensory analyses of fresh meat (and other foods) include standardizing the terms used to describe their flavor. Similar terms might have different meanings for different people. For example, one of the challenges that we encountered while developing the meat lexicon was that we would ask people: "What does this piece of meat taste like?" And they would answer: "It tastes "beefy." So, what does the term "beefy" really mean? Can we create a language that describes the underlying notes that contribute to the flavor of beef in the way the flavors of olive oil or wine are described? Having a lexicon helps in identifying the different notes that contribute to the "beefy" flavor.

Q: In terms of fat content and types of fats, what are the differences between pasture- and grain-fed beef? Do these influence the respective flavor profiles?

Our research (Tansawat *et al*., 2013) has shown that pasture-fed beef has significantly lower amounts of palmitic acid and oleic acid but higher amounts of polyunsaturated fatty acids (PUFA) such as linoleic acid, alpha linolenic acid, arachidonic acid, eicosapentaenoic acid, docosapentaenoic acid, and docosahexaenoic acid. In terms of total fat content, grain-fed beef has approximately 12% fat while

grass-fed beef has approximately 3% fat. Furthermore, changes in beef fatty acid composition occurs with intramuscular fat content changes because of the preferential deposition of saturated and monounsaturated fatty acids (SFA and MUFA) due to rumen biohydrogenation. In the end, grain-fed beef tends to have greater amounts of fat and more stable fats. Greater fat content may improve the texture, juiciness, and mouthfeel of grain-fed beef. Meanwhile, grass-finished beef is more prone to off-flavors and off-odors due to greater proportions of less stable PUFA.

Q: What are the common sensory attributes of both pasture- and grain-fed beef? Which attributes differentiate them?

Our work has shown that the common attributes between pasture and grain-fed beef were astringent, bloody, brothy, browned, fatty, livery, metallic, oxidized, roast beef, salty, sour, and sweet. Pasture-fed beef was rated higher in barny, bitter, gamey, grassy, and lower in umami and juicy (Maughan *et al*., 2012).

Q: What are your findings when relating meat flavor profile with consumer acceptance of grain and grass-fed beef?

Utah consumers preferred grain-fed beef. Their preference for these samples was associated with terms such as salty, juicy, fatty, sweet, bloody, umami, brothy, roast beef, and browned (Maughan *et al*., 2012). However, it is important to note that consumer preferences might change with demographics. For example, different results might be obtained if the same test was performed in Europe, Asia, or Latin America.

Q: Do you think that market trends and/or ethical concerns (e.g., healthful eating trends, free-grazing, humane treatment of animals) have an impact on consumer perceptions of grass-fed beef?

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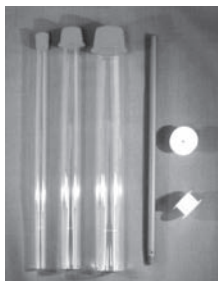

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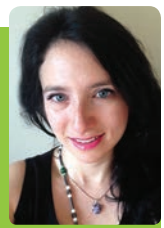
I believe that market trends have impacted the overall perception of pasture-fed beef. Consumers might choose this type of beef based not only on its flavor profile but also on its nutritional properties. However, when consumers are asked to rate attributes of importance they have historically ranked price and flavor attributes as most important. Recent work at Utah State University supports this sentiment. Price was the number one purchasing motivator, while production practices were less important to consumers (Chail *et al*., 2016).

Q: How does the type of grass-finishing impact beef flavor?

Some of our recent work has indicated that not all forages utilized for grass-finishing are equal. Birdsfoot trefoil, a perennial legume containing greater amounts of dietary carbohydrates, was evaluated by consumers and determined to have comparable tenderness and juiciness with grain-fed beef (Chail *et al*., 2016). Meanwhile, flavor liking was rated lower. We believe that this was due to the fact that the fatty acid composition of the legume-fed beef was more in line with grass-fed beef. While the importance of fatty acids to flavor is certainly well known, we are currently diving deeper looking at how fatty acids change during cooking. In the end, we hope to have a better understanding of how initial fatty acid composition influences the development of flavor and flavor compounds.

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



PATENTS

Lipid composition for the prevention or treatment of skin problems

Griinari, M. and I. Bruheim, Clanet Oy, US9375414, June 28, 2016

The invention relates to a novel lipid composition. Further, the invention relates to the use of a lipid composition for the treatment, alleviation, and prevention of skin problems.

Neutralizing hair composition

Obukowho, P., Spartan Brands Inc., US9420862, August 23, 2016

A method, composition, and kit for straightening human hair. The method comprises applying an alkali relaxer to the hair and then neutralizing the hair with a hair neutralizing composition comprising at least one fatty acid or a quaternary derivative thereof. The kit comprises an alkali hair relaxer or components for preparing such a relaxer and the hair neutralizing composition.

Lipase-containing polymeric coatings for the facilitated removal of fingerprints

Buthe, A., *et al.*, Toyota Motor Corp, Univ. of Minnesota, US9428740, August 30, 2016

A substrate or coating is provided that includes a lipase with enzymatic activity toward a component of a fingerprint. Also provided is a process for facilitating the removal of fingerprints is provided wherein an inventive substrate or coating including a lipase is capable of enzymatically degrading of one or more components of the fingerprint to facilitate fingerprint removal from the substrate or said coating. Applying heat to the substrate or coating increases the rate of fingerprint removal.

Process for producing a baked product having increased flavor stability with catalase and phospholipase

Bennedbaek-Jensen, S.L. and O. Henrik, Novozymes AS, US9402402, August 2, 2016

The present invention relates to a process for producing a baked product having increased flavor stability comprising the steps of: (a) preparing a dough comprising flour, water, an enzyme preparation having catalase activity, and an enzyme preparation having phospholipase activity; and (b) baking the dough to obtain the baked product.

Toughening cross-linked thermosets

Palmese, G.R., *et al.,* Univ Drexel, US Army, US Government, US9394427, July 19, 2016

Grafted triglycerides comprising an acrylated triglyceride grafted with a fatty acid residue containing 4 to 28 carbon atoms. Also described are methods for making a grafted triglyceride and for curing a material selected from vinyl esters and unsaturated polyesters and mixtures thereof and optionally a reactive diluent. The method includes the steps of mixing a grafted triglyceride of the present invention with a material selected from vinyl esters, unsaturated polyesters and mixtures thereof to form a mixture, and curing the mixture to form a cured resin system. A cured resin system comprising a cured product obtained by the foregoing method and composites containing the cured product and a filler or reinforcing material are also disclosed. This method also includes use of the grafted triglycerides to make toughened resin and composite systems with reduced hazardous air pollutants without significantly reducing the glass transition temperature and significantly increasing the viscosity.

Heat-tolerant, lipid-based filling

Schulok, J. and C. Richard, Intercontinental Great Brands LLC, US9351501, May 31, 2016

Methods and compositions for a lipid-based food filling including a lipid system, and particulates having a size of about 30 μm or less, the particulates having a lipophilic surface, wherein the filling has a water activity of less than about 0.3 and wherein substantially no fat separates from the filling when the filling is heated to temperatures of up to about 200˚F.

Method for production of an emulsion

Bongers, P.M.M., *et al,* Conopco Inc., US9352289, May 31, 2016

The present invention has as an objective to provide a new emulsification method which can produce concentrated water-continuous emulsion containing lipophilic compounds in a dispersed phase, with a very fine dispersed phase droplet size less than a micron, and a narrow size distribution of the dispersed phase. This objective has been met by a method wherein a water-continuous emulsion is made using a controlled deformation dynamic mixer or a cavity transfer mixer.

Pressure-sensitive adhesives, coatings, and films from plant oils

Sun, X.S., *et al.*, Kansas State Univ. Res Found, US9441112, September 13, 2016

Compositions useful for preparing pressure-sensitive adhesives, coatings, and/or films are provided, along with methods of making and using the same. The compositions are made from renewable, plant-based materials. The compositions comprise plant oil triglycerides that are polymerized and crosslinked to yield polymer matrices. Plant-based carriers and/or tackifiers can be used in the invention, including epoxidized plant oil triglycerides, acry-

lated epoxidized plant oil triglycerides, and dihydroxylated plant oil triglycerides. Natural tackifiers such as rosin esters and terpenes can also be used in the compositions. Dihydroxylated plant oil triglyceride tackifiers for use in biobased and synthetic adhesives are also provided.

Use of at least one coproduct from the vegetable oil refining industry for obtaining a purified total unsaponifiable vegetable oil product

Legrand, J., *et al.,* US9447361, September 20, 2016

The present invention relates to the use of at least one vegetable oil refining industry by-product to obtain a purified total unsaponifiable of vegetable oil cleared of the impurities initially present in the said by-product, advantageously cleared of sapid and odorous compounds and/or chemical compounds resulting from the deterioration and the degradation of vegetable oils. The invention further relates to a method for obtaining a purified total unsaponifiable of vegetable oil from at least one vegetable oil refining industry by-product. The invention further relates to a purified total unsaponifiable of vegetable oil able to be obtained by this method, as well as compositions containing such an unsaponifiable. The invention further relates to such unsaponifiables or such compositions for the use thereof as a drug, medical device, dermatological agent, cosmetic agent, or nutraceutical, in humans or animals.

Palm-based fractionated oil and fat, oil and fat composition, and food product containing the same

Sadakane, T., *et al.,* J. Oil Mills Inc., US9370196, June 21, 2016

An oil and fat composition is provided having superior operability and processability, in terms of a liquefying phenomenon of sugar, tackiness, and texture of fried doughnuts; filling condition and hardness of shortening; and solidifying time of coating chocolate, by the superior crystallization-promoting effect. A palm-based fractionated oil and fat has 70–90% by weight of the tripalmitin content to triglyceride and 1–8% by weight of the unsaturated fatty acid content to total fatty acid. The oil and fat comprises a hard part obtained by, for example, performing a crystallization operation of palm super stearin with iodine value 10–17 so that the slurry SFC is 20% or less, and fractionating the slurry so that the hard part yield is 26% by weight or less. The fractionation is preferably performed so that a numerical value of the hard part yield/the slurry SFC is 10 or less.

Organic functionalization of layered double hydroxides

Puhala, A.S. and L. Xiaofan, Flow Polymers LLC, US9410031, August 9, 2016

The present invention relates to a method for preparing an organically functionalized layered double hydroxide which comprises reacting (a) a layered double hydroxide, (b) a triglyceride oil, (c) an enzyme which is capable of catalyzing the hydrolysis of an ester, and (d) water, to produce the organically functionalized layered double hydroxide. The subject invention further reveals a method for preparing an organically functionalized layered double hydroxide which comprises (1) dispersing into an aqueous medium (a) the layered double hydroxide, (b) the triglyceride oil, and (c) the enzyme; (2) allowing the triglyceride oil to hydrolyze into long-chain fatty acids and glycerol to produce a dispersion of the organically functionalized layered double hydroxide; and (3) recovering the organically functionalized layered double hydroxide from the aqueous dispersion.

Fatty acid composition and plant extract and pharmaceutical preparation and application thereof

Xing, J., *et al.*, US9446083, September 20, 2016

A fatty acid composition containing linoleic acid, linolenic acid, and oleic acid is provided. Also provided is a fatty acid composition containing linoleic acid, linolenic acid, oleic acid, and at least one selected from palmitinic acid, palmitoleic acid, stearic acid, arachidic acid, and docosanoic acid. A plant extract and a pharmaceutical preparation are provided, wherein the pharmaceutical preparation contains an active component including at least one of the fatty acid composition, the plant extract and modified products thereof. Also provided is an application of the fatty acid composition, the plant extract and the pharmaceutical preparation in multiple fields. The pharmaceutical preparation may function to repair various wounds and traumas in skin, mucosa, lumina, and muscular tissues.

Genetically-engineered microbial oil dielectric fluid

Han, S.J. and B.R. Maurer, Dow Global Technologies LLC, US9362980, June 7, 2016

The present disclosure provides a dielectric fluid composed of a genetically engineered microbial oil (GEMO) and an antioxidant. The GEMO includes a triglyceride and an amount of small glyceride. The amount of small glyceride is within a range from 0.1 weight percent to 30 weight percent, based upon the GEMO weight.

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

EXTRACTS & DISTILLATES

Production of 7,8-dihydroxy unsaturated fatty acids from plant oils by whole recombinant cells expressing 7,8-linoleate diol synthase from *Glomerella cingulata*

Seo, M.-Ju., *et al.*, *J. Agric. Food Chem. 64*: 8555–8562, 2016, http://dx.doi.org/10.1021/acs.jafc.6b03497.

The reaction conditions for the production of 7*S*,8*S*-dihydroxy-9,12(*Z*,*Z*)-octadecadienoic acid from linoleic acid by recombinant *Escherichia coli* expressing 7,8-linoleate diol synthase from *Glomerella cingulata* were optimized using response surface methodology. The optimal reaction conditions were pH 7.0, 18.6°C, 10.8% (v/v) dimethyl sulfoxide, 44.9 g/L cells, and 14.3 g/L linoleic acid, with agitation at 256 rpm. Under these conditions, recombinant cells produced 7,8-dihydroxy unsaturated fatty acids in the range of 7.0–9.8 g/L from 14.3 g/L linoleic acid, 14.3 g/L oleic acid, and plant oil hydrolysates such as waste oil and olive oil containing 14.3 g/L linoleic acid or oleic acid. To the best of the authors' knowledge, this is the first report on the biotechnological production of 7,8-dihydroxy unsaturated fatty acids.

Olive oil authentication, traceability and adulteration detection using DNA-based approaches

Kalaitzis, P. and Z. El-Zein, *Lipid Technol. 28*: 173–176, 2016, http://dx.doi.org/10.1002/lite.201600048.

Olive oil is the fresh juice produced by pressing olive fruits. It serves as the main component of the Mediterranean diet and one of the most valuable products of the agro-food industry, not only for its taste, but also for its high nutritional value. As it is considered the lipid constituent of the olive fruits, it is composed mainly of triglycerides and phenolics. Authentication and traceability of extra virgin olive oil is a challenging research task due to the complexity of fraudulent practices. Various chemical and biochemical techniques have been developed for determining the authenticity of olive oil. Olive oil DNA-based analyses have gained attention in recent years, due to high specificity, sensitivity and reliability. DNA analyses have very high discriminating power because ultimately the unique identity of a variety or species is to a great extent genetically dependent. Polymorphisms are genetic variations which refer to the variation in populations or species. Molecular markers provide information on genetic variations and are valuable tools to determine olive oil authenticity. Molecular markers such as SNPs, microsatellites, SCARs and AFLPs have been used for the identification of the varietal origin of olive oils. This feature provides an overview of the current trends and critical issues on DNA-targeted approaches used for traceability and authenticity of olive oil.

Molecular characterization and anti-inflammatory activity of galactosylglycerides and galactosylceramides from the microalga *Isochrysis galbana*

de los Reyes, C., *et al.*, *J. Agric. Food Chem. 64*: 8783–8794, 2016, http://dx.doi.org/10.1021/acs.jafc.6b03931.

Isochrysis galbana is a marine microalga rich in PUFAs that is widely used as feed in aquaculture and more recently investigated for its potential in food applications and as source of bioactive compounds. In this study, the biomass obtained from cultures of *I. galbana* has been investigated to determine its content in glycosylglycerides and glycosylceramides. By using NMR, UPLC-MS/MS, and fatty acid profiles, the structures of ten monogalactosyldiacylglycerols (MGDGs 1–10) and nine digalactosyldiacylglycerols (DGDGs 11–19) have been established. Two distinctive features of the galactosylglycerides from *I. galbana* are the wide presence of highly unsaturated acyl chains derived from stearidonic acid ($18{:}4\Delta^{6Z,9Z,12Z,15Z}$) and octadecapentaenoic acid ($18{:}5\Delta^{3Z,6Z,9Z,12Z,15Z}$), as well as the unusual coexistence of αβ-DGDGs and ββ-DGDGs. Three new galactosylceramides, isogalbamides A-C (20–22), have also been isolated and characterized by NMR and MS/MS. These metabolites, which are the first galactosylceramides described from microalgae, derive from unprecedented tetraolefinic sphingoid bases. In anti-inflammatory assays, the MGDG and DGDG mixtures and the isolated DGDGs 11 and 12 showed significant activity as inhibitors of the production of the pro-inflammatory cytokine TNF-α in lipopolysaccharide-stimulated human THP-1 macrophages, while the galactosylceramides showed moderated activity.

Formation of 3-MCPD Fatty acid esters from monostearoyl glycerol and the thermal stability of 3-MCPD monoesters

Zhao, Y., *et al.*, *J. Agric. Food Chem. 64*: 8918–8926, 2016, http://dx.doi.org/10.1021/acs.jafc.6b04048.

Formation of 3-monochloropropanediol (3-MCPD) esters from monostearoyl glycerol (MSG) was investigated under high temperature and low moisture conditions. Different organic and inorganic chlorides, including lindane, KCl, $CaCl_2$, NaCl, $MgCl_2$, $AlCl_3$, $CuCl_2$, $MnCl_2$, $SnCl_2$, $ZnCl_2$, and $FeCl_3$, were evaluated for their potential to react with MSG to form 3-MCPD and glycidyl esters at 120 and 240°C using a UPLC-Q-TOF MS analysis. The results indicated that different chlorine compounds differed

in their capacity to react with MSG and formed different products including 3-MCPD mono- and diesters, distearoylglycerol, and glycidyl esters. According to electron spin resonance (ESR) and Fourier transform infrared (FT-IR) spectroscopies, free radical mediated formation mechanisms involving either five-membered or six-membered cyclic acyloxonium free radicals (CAFR) from monoacylglycerol (MAG) were proposed. Tandem quadrupole-time-of-flight (Q-TOF) MS and MS/MS analyses confirmed the free radical mechanisms. In addition, the results from the present study showed that 3-MCPD monoester could be degraded upon thermal treatment and suggested a possible catalytic role of Fe^{3+} under the experimental conditions.

Identification of acyl chain oxidation products upon thermal treatment of a mixture of phytosteryl/-stanyl linoleates

Wocheslander, S., *et al.*, *J. Agric. Food Chem. 64*: 9214–9223, 2016, http://dx.doi.org/10.1021/acs.jafc.6b04326.

A mixture of phytosterols/-stanols, consisting of 75% β-sitosterol, 12% sitostanol, 10% campesterol, 2% campestanol, and 1% others, was esterified with linoleic acid. The resulting mixture of phytosteryl/-stanyl linoleates was subjected to thermal oxidation at 180°C for 40 min. A silica solid-phase extraction was applied to separate a fraction containing the nonoxidized linoleates and nonpolar degradation products (heptanoates, octanoates) from polar oxidation products (oxo- and hydroxyalkanoates). In total, 15 sitosteryl, sitostanyl, and campesteryl esters, resulting from oxidation of the acyl chain, could be identified by GC-FID/MS. Synthetic routes were described for authentic reference compounds of phytosteryl/-stanyl 7-hydroxyheptanoates, 8-hydroxyoctanoates, 7-oxoheptanoates, 8-oxooctanoates, and 9-oxononanoates, which were characterized by GC-MS and two-dimensional NMR spectroscopy. The study provides data on the formation and identities of previously unreported classes of acyl chain oxidation products upon thermal treatment of phytosteryl/-stanyl fatty acid esters.

Relationship between chocolate microstructure, oil migration, and fat bloom in filled chocolates

Delbaere, C., *et al.*, *Eur. J. Lipid Sci.Technol.118*: 1800–1826, 2016, http://dx.doi.org/10.1002/ejlt.201600164.

Fat bloom is one of the main quality problems in the chocolate industry. A bloomed chocolate product is characterized by the loss of its initial gloss and the formation of a gray-whitish haze, which makes the product unappealing from a consumer point of view. In the industry, most of the fat bloom related problems arise in filled chocolate products, like pralines and chocolate-coated biscuits. In these products, oil migration is considered the main cause of fat bloom development. It leads to the dissolution of solid cocoa butter crystals in the chocolate shell which may recrystallize with the formation of undesired crystals. These give rise, upon growth, to visual fat bloom. When looking at the available literature, most of the studies elucidate the possible mechanisms of oil migration and the subsequent fat bloom formation using model systems. These model systems are sometimes too distant from the real industrial applications and the important role of the microstructure of the products are often neglected, although it plays a crucial role in migration-induced fat bloom development. The main objective of this review is to describe the relationships between chocolate microstructure, oil migration, and fat bloom.

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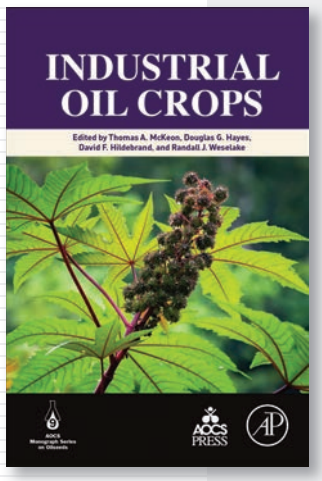

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Industrial Oil Crops

AOCS Monograph Series on Oilseeds, Volume 9

Edited by Thomas A. McKeon, Douglas G. Hayes, David F. Hildebrand, and Randall J. Weselake

March 2016 | ISBN 9781893997981 | 460 pages | Available in print and ebook

Industrial Oil Crops presents the latest information on important products derived from seed and other plant oils, their quality, the potential environmental benefit, and the latest trends in industrial uses. This book provides a comprehensive review of key oil crops that provide products used for fuel, surfactants, paints and coatings, lubricants, high-value polymers, safe plasticizers and numerous other products. Led by an international team of expert editors, this book will be a valuable asset for those in product research and development as well as basic plant research related to oil crops.

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The feasibility of wax-based oleogel as a potential co-structurant with palm oil in low-saturated fat confectionery fillings

Doan, C.D., *et al.*, *Eur. J. Lipid Sci. Technol. 118*: 1903–1914, 2016, http://dx.doi.org/10.1002/ejlt.201500172.

In this research, food-grade oleogels (differing in concentration of bees wax in rice bran oil) were combined with palm oil at three replacement levels (17, 33, and 50%wt) to form a continuous fat phase reduced in saturated fatty acids. We explored the crystallization and gelling behavior of the wax-based palm-blend mixtures, and those of the fillings containing sugar and hazelnut particles dispersed in these wax-based palm-blend fat phases. The wax-based palm-blends were different in chemical nature (unique triacylglycerols in hazelnut oil, rice bran oil, and palm oil; fatty esters, *n*-alkanes, free fatty acids, and free fatty alcohols in bees wax), resulting in the formation of different crystalline morphologies when oleogels and palm oil were crystallized together. The crystallization of BW-oleogel has proven its contribution to the gelation of the hybrid mixtures during the instant cooling step. The maximum amount of palm oil being replaced by wax-based oleogels was 17%, resulting in a system having similar gel strength with the reference (100% of palm oil). The gel strength obtained from rheological measurements was explained based on the information obtained from oil binding capacity, microstructure (polarized light microscopy), and thermal studies. The dilution effect was observed and the melting enthalpy decreased with the increasing oleogel fraction. The solid fat content of the final filling products at body temperature was lower than 2.0%wt, suggesting a non-waxy mouthfeel. This research provides imperative information involved in the use of oleogels for the engineering of low saturated-fat confectionery products.

Synthesis and low temperature characterization of iso-oleic ester derivatives

Ngo, H., *et al.*, *Eur. J. Lipid Sci. Technol. 118*: 1915–1925, 2016, http://dx.doi.org/10.1002/ejlt.201500468.

Three new iso-oleic ester derivatives (i.e., isopropyl ester (IOA-iPrE, 6), n-butyl ester (IOA-n-BuE, 7), and 2-ethylhexyl ester (IOA-2-EHE, 8)) were synthesized from iso-oleic acid (IOA, 4) using a standard esterification method. These esterified alcohols were chosen because of their bulky and branched-chain alkyl groups which can reduce melting point in comparison to a smaller alkyl group such as methyl ester. The differential scanning calorimetry (DSC), cloud point and pour point results showed that esters 6, 7, and 8 had much lower melting transition temperatures and cold flow properties than the methyl (IOA–FAME, 5) and parent 4. The oxidative and thermal stability by pressure (P-DSC) and thermogravimetric analysis (TGA) results also showed a very similar trend where the bulkier and branched-chain alkyl esters had better stability than the smaller headgroup esters.

Study of correlations between composition and physicochemical properties during methylic and ethylic biodiesel synthesis

da Silva, F.L., *et al.*, *Ind. Crops Prod. 95*: 18–26, 2017, http://dx.doi.org/10.1016/j.indcrop.2016.09.053.

In this work, correlations between the physicochemical parameters (density and kinematic viscosity) and the composition of various samples, obtained during the biodiesel production process of methylic and ethylic soybean biodiesel, were investigated. The results point out that the composition of the medium in terms of remaining catalyst and its residues, alcohol and water content, among others variables, has no significant influence on the physicochemical properties studied. These findings are mainly influenced by the composition of the medium in terms of FAAE, TAG, DAG and MAG.

Esterification of free fatty acids in non-edible oils using partially sulfonated polystyrene for biodiesel feedstock

Suresh, R., *et al.*, *Ind. Crops Prod. 95*: 66–74, 2017, http://dx.doi.org/10.1016/j.indcrop.2016.09.060.

Partially sulfonated polystyrene (PSS), synthesized from expanded polystyrene waste (EPS), was used as a catalyst for free fatty acid (FFA) conversion in non-edible oils. Acidic and water absorbing properties of the PSS facilitated the catalytic action for the FFA conversion by esterification reaction. The reaction was done on simulated acid oil (WCO) containing oleic acid and sunflower oil, and rubber seed oil (RSO). Effects of temperature, catalyst amount and alcohol to acid molar ratio were studied. FFA conversion increased with each of these factors. The advantage of this heterogeneous catalyst is that it is efficient as commercial ion exchange resin and easily removable from the reaction mixture. PSS is found to substantially reduce the acid value of WCO and RSO from 17 to 3.2 mg KOH/g and from 28.8 to 4.8 mg KOH/g respectively at 75°C. The WCO and RSO with reduced acid value may be used as a feedstock for biodiesel production.

Industrial Applications

Supercritical CO_2 oilseed extraction in multi-vessel plants. 3. Effect of extraction pressure and plant size on production cost

Núñez, G.A., *et al.*, *J. Supercrit. Fluids*, online November 2016, http://dx.doi.org/10.1016/j.supflu.2016.11.002.

This work completes a series of three studies about the estimation of the cost of extracting vegetable oil from seeds using supercritical CO_2. The focus of this work was determining the effect of extraction pressure (30, 50, and 70 MPa) in the production cost of

a supercritical CO_2 extraction of a packed bed of 2-mm oilseeds in plants with two-extraction vessels with aspect ratio of 4.5, using a superficial velocity of 5 mm/s. When extraction pressure increased while keeping other variables constant, production cost decreased. For 2×1 m^3 extraction plants, increasing extraction pressure from 30 to 50 MPa decreased production cost 30.9%, but when extraction pressure further increased from 50 to 70 MPa production cost only decreased 9.9%. Results suggest that the recommended extraction pressure for oilseed extraction is 50 MPa. Also, this work compared plants operating at the three extraction pressures when annual productivity was kept constant (231, 456, or 596 ton of oil per year). The total extraction volume of the plant diminished as the extraction pressure increased. Optimum production cost in these cases was quite similar for plants operating at 30, 50, and 70 MPa, but the total volume of the plant decreased 63.6% when increasing extraction pressure from 30 to 50 MPa for the plant producing 456 ton of oil per year, and an additional 31% when increasing it from 50 to 70 MPa. The lowest production cost estimated was 5.52 USD per kg of oil (optimum extraction time of 2.75 h) in a 4×1 m^3 plant processing 2-mm prepressed oilseeds, and operating at 40°C and 50 MPa. The manuscript includes a sensitivity analysis on production cost as a function of a variation of ±50% of uncertain variables cost (respect to nominal values), which were considered as constant in our previous contributions. That cost items were unitary cost of annual labor, CO_2, and substrate, being the variation of the last one the more significant effect on production cost.

Potential pyrolysis pathway assessment for microalgae-based aviation fuel based on energy conversion efficiency and life cycle

Guo, F., *et al.*, *Energy Convers. Manage. 132*: 272–280, 2017, http://dx.doi.org/10.1016/j.enconman.2016.11.020.

Although the research of microalgae pyrolysis has been conducted for many years, there is a lack of investigations on energy efficiency and life cycle assessment. In this study, we investigated the biocrude yield and energy efficiency of direct pyrolysis, microalgae residue pyrolysis after lipid extraction (indirect pyrolysis), and different microalgae co-pyrolysis. This research also investigated the life cycle assessment of the three different pyrolysis pathways. A system boundary of Well-to-Wake (WTWa) was defined and included sub-process models, such as feedstock production, fuel production and pump-to-wheels (PTW) stages. The pathway of *Isochrysis* indirect pyrolysis shows the best performance in the mass ratio and energy ratio, produces the most kerosene component precursor, has the lowest WTWa total energy input, fossil fuel consumption and greenhouse gas emissions, and resultes in the best energy efficiency. All the evidence indicates that *Isochrysis* R2 pathway is a potential and optimal pyrolysis pathway to liquid biofuels. The mass ratio of pyrolysis biocrude is shown to be the decisive factor for different microalgae species. The sensitivity analysis results also indicates that the life cycle indicators are particularly sensitive to the mass ratio of pyrolysis biocrude for microalgae-based hydrotreated pyrolysis aviation fuel.

Sustainable green solvents and techniques for lipid extraction from microalgae: a review

SPJ Kumar, *et al.*, *Algal Res. 21*: 138–147, 2017, http://dx.doi.org/10.1016/j.algal2016.11.014.

Energy security is a serious concern for a sustainable economy where it has necessitated alternative renewable energy that can have the potential to meet the futuristic needs. Among renewable energies, carbon neutral biofuels from microalgae appear to be a promising move towards sustainability and cleaner fuels owing to its attributes of high CO_2-sequestering capability, high lipid productivity and being easily cultivable in an open pond and waste/marine/brackish water. However, the commercial viability of algae-based fuels suffers mainly from the cost incurred during the process. Among the steps involved in the biodiesel production from microalgae, lipid extraction in particular consumes not only a significant amount of energy and time but also causes environmental contamination by usage of toxic solvents. Conventional solvents used in lipid extraction process may further aggravate the quality of the product by dissolving other compounds like chlorophyll that may lead to erroneous results of lipid content. To circumvent the problem, green solvents and process intensification methods/techniques (green extraction technologies) potentially improve the characteristics of energy reduction, eco-friendliness, non-toxicity and efficient lipid extraction. Hence, this review focuses on the prospects of green solvents and extraction techniques that could improve the commercial viability of biodiesel production.

Synthetic Biology

Current status in biotechnological production and applications of glycolipid biosurfactants

Paulino, B.N., *et al.*, *Appl. Microbiol. Biotechnol.* 100: 10265–10293, 2017, http://dx.doi.org/10.1007/s00253-016-7980-z.

Biosurfactants are natural compounds with surface activity and emulsifying properties produced by several types of microorganisms and have been considered an interesting alternative to synthetic surfactants. Glycolipids are promising biosurfactants, due to low toxicity, biodegradability, and chemical stability in different conditions and also because they have many biological activities, allowing wide applications in different fields. In this review, we addressed general information about families of glycolipids, rhamnolipids, sophorolipids, mannosylerythritol lipids, and trehalose lipids, describing their chemical and surface characteristics, recent studies using alternative substrates, and new strategies to improve of production, beyond their specificities. We focus in providing recent developments and trends in biotechnological process and medical and industrial applications.

A chat with **AOCS Lipid Library's** new **Editor-in-Chief**

The AOCS Lipid Library *(http://lipidlibrary.aocs.org/) is a leading online source of information related to lipid science and technology. The Open Access site, which averages nearly 300,000 visitors a year, is a free resource for students, technologists, scientists, and laypersons to learn about lipid chemistry and technology via a less-technical, abbreviated format that is easy to read and understand. The Library's new Editor-in-Chief, Alejandro Marangoni, is a professor and Tier I Canada Research Chair Food, Health and Aging at the University of Guelph, Canada, and a Fellow of the Royal Society of Chemistry. Marangoni's work concentrates on the materials science of soft matter. He has published over 300 refereed research articles, 60 book chapters, 13 books, and over 40 patents. He has received many awards, including the 2013 AOCS Stephen Chang award, the 2014 IFT Chang Award in Lipid Science, the 2014 Supelco/Nicholas Pelick Award, and the 2015 ISF Kaufmann Medal. Marangoni was honored as one of the 10 most influential Hispanic Canadians in 2012, and a Fellow of the American Oil Chemists' Society in 2015. He is the first co-editor in Chief of Current Opinion in Food Science and Technology, and past Editor-in-Chief of Food Research International. Here, Marangoni talks about his vision and plans for the Library.*

Q: Why is the AOCS Lipid Library (LL) important, and what are some opportunities for further development?

The LL is one of the most important contributions that AOCS makes to our global community. It can become the repository of all the knowledge related to lipid science, fats and oils in particular. The content is top-notch and freely available to everyone around the world. We need to increase the scope of the LL, expand and improve its content, and open it up to contributions from AOCS members, other societies, and more. I see the potential to draw members of other societies into the AOCS fold through the LL.

Q: What role has the Library played in your own education and career, and those of your students?

My graduate students always use the LL to take their first steps in the field of fats and oils. I know of many overseas students who have used this resource for years in their respective countries. We need to expand its scope and content to make it even more useful. I use the Lipid Physics section often, since it is there and readily available!

Q: What was the most important thing you ever learned from the Library?

That knowledge is power

Q: What is your vision for the site, and how do you plan to achieve it?

Many, many changes and improvements are forthcoming. Streamlining the Associate Editor roster is a top priority. We also want to make sure that all current AEs are ready to give serious attention to this role, since we need to improve and expand our library. Editorship and authorship of the LL is a voluntary function; nobody gets paid here. After a few years as AE, many may have had enough and would rather pass on the baton to a fresh group. Others may be ready to rock'n roll again. New appointments, some shuffling, some focusing are all happening this year. I think an LLA (Lipid Library Author) designation should be offered for authors after three or more contributions to LL by an author every three years. This could be highlighted in several possible ways, including special mentions on the LL site, in *Inform* magazine, at the AOCS Annual Meeting, or a combination of these.

Q: Keeping current is always a challenge. How will you make sure that fresh information keeps being added and older information is updated?

A new "working group" of three Assistant EIC's will be created, so that deadlines are met and the ship keeps moving swiftly in the defined direction. We will be relentless and will take no prisoners.

Q: Lipid science and technology touch so many fields and levels of expertise. Are there topics or areas that are currently underrepresented?

Many areas are thin and incomplete. If you have used the library, you probably have noticed. We will fill these gaps in the coming year.

Q: How will you insure that the Library offers leading information in subject areas that are less familiar to you?

The function of the Associate Editors is critical. We currently have and will be appointing interested individuals who share the vision, have the expertise, and are willing to put in the time. This is NOT an honorary position; it is a working position.

Q: What resources, both technological and human, will be needed to further develop the Library?

We need easier and more effective ways of posting content. I wish it would work as Wikipedia does……I think we need to open it up.

Q: What should people do if they want to contribute to or help with the Library?

Do not worry, if you want to work, we have work for you. Call me at your own risk. If you see me walking toward you at the Annual Meeting, run.

Structured lipids for food and nutraceutical applications

Lipid Snippets is a regular Inform column that features select content from The AOCS Lipid Library (http://lipidlibrary.aocs.org/).

Molly J. Sproston, Ebenezer A. Ifeduba, and Casimir C. Akoh

Excerpted from http://dx.doi.org/10.21748/lipidlibrary.41522

Structured lipids (SLs) are lipids that have been modified from their natural form for specific food and nutraceutical applications. This modification involves a change in the chemical structure of the lipid brought about by addition or rearrangement of fatty acids on the glycerol backbone [1].

The starting material can be acylglycerols or phospholipids (PLs) and modifications may be carried out using chemical catalysts or enzymes (biocatalysts). Chemical modification is commonly used in industry, but only randomized products can be made. Enzymatic modification is advantageous because only mild reaction conditions are required, minimal byproduct formation improves product yield, and the specificity of lipases allow for better control over product characteristics and applications [2].

There has been growing interest in the use of enzymes to produce SLs with nutritional and functional benefits and examples are summarized in Table 1. SL products include medium and long chain triacylglycerols (MLCTs), human milk fat (HMF) analogues, cocoa butter substitutes, reduced calorie and *trans*-free fats, monoacylglycerols (MAGs), diacylglycerols (DAGs), and modified PLs.

SLs may be produced via different reaction types. Acidolysis reactions involve the incorporation of fatty acyl groups from free fatty acids (FFAs) to triacylglycerol (TAG) molecules. Interesterification reactions involve exchange of fatty acyl groups between two or more TAG molecules. Alcoholysis is a substitution reaction in which fatty acyl groups from TAG molecules are transferred to an alcohol such as glycerol (glycerolysis) or ethanol (ethanolysis) [3]. The reaction schematics can be seen at http://lipidlibrary.aocs.org/History/content.cfm?ItemNumber=41522. Both chemical and enzymatic interesterification reactions can take place in a batch reactor where all substrates and catalyst are added and stirred over time, and also in continuous reactors where catalysts are continuously added to substrates to reduce mass transfer limitations [3,4].

Chemical interesterification is used widely in industry because it is relatively inexpensive compared to using enzymes; however, only randomized products can be produced as previously mentioned. The reaction involves hydrolysis of TAG molecules into FFAs followed by reesterification of the FFAs onto the glycerol backbone. This reaction is catalyzed by alkali metals or metal alkylates under anhydrous conditions at high temperatures. Water must be continuously removed to prevent undesired hydrolysis and maximize reaction yield. Commonly, sodium methoxide is used because it is inexpensive and can react at lower temperatures [3].

For enzymatic modification, lipases and phospholipases are the preferred enzymes to use as biocatalysts to modify fats and oils. They selectively hydrolyze fatty acids on TAG substrate and then re-esterify the glycerol with a new fatty acid while in a hydrophobic environment. Lipases can be used

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for acidolysis, interesterification, and alcoholysis reactions, and reactions can occur in organic solvent or a solvent-free medium. Different enzymes can be used to achieve certain TAG structures.

Non-specific enzymes randomly hydrolyze fatty acids on TAG molecules while *sn*-1,3-specific enzymes preferentially hydrolyze fatty acids on the *sn*-1 and 3 positions. *Candida rugosa* and *Candida antarctica* (Novozym 435) lipases are examples of non-specific enzymes, while *Rhizomucor miehei* (Lipozyme RM IM) and *Thermomyces lanuginosus* (Lipozyme TL IM) lipases are *sn*-1,3-specific enzymes where the names in parenthesis represents commercially available immobilized versions. Immobilization on supports such as silica gel or acrylic resins allows for recovery and reuse of enzyme over time as well as increased thermal stability [2].

The authors are with the Department of Food Science and Technology, University of Georgia, Athens, Georgia, USA.

TABLE 1. Some uses, effects, possible methods, and desired compositions of various structured lipids[a]

Product Type	Uses and Effects	Potential Methods for Synthesis	Desired Composition
Medium and Long Chain Triacylglycerols (MLCTs)	• Parenteral and enteral feeding • Rapid energy source • Treatments of lipid mal-absorption and metabolic syndromes	Acidolysis of long chain TAGs with medium chain FFAs using *sn*-1,3-specific lipases	*sn*-MLM TAGs
Human Milk Fat (HMF) Analogues	• Infant Formula • Infant formula enriched with ARA, DHA, and MCFAs • Increased lipid absorption for infants	Interesterification/acidolysis of high oleic TAGs/ FFAs and oils with palmitic acid located at the *sn*-2 using *sn*-1,3-specific lipases	*sn*-OPO TAGs and other TAGs containing ARA, DHA, and MCFAs
Cocoa Butter Alternatives	• Chocolate • Confectionaries • Bakery products	Acidolysis of vegetable oils high in oleic acid at the *sn*-2 position and palmitic and stearic FFAs using *sn*-1,3-specific lipases	*sn*-POP TAGs *sn*-StOSt TAGs *sn*-POSt TAGs
Reduced Calorie Fats and Low trans/trans-free Fats	• Snack foods • trans-Free margarines • Shortenings • Sauces • Baked chips • Baked goods • Reduces health implications of trans-fatty acids	Interesterification of SCFA TAGs with LCFA TAGs Enzymatic interesterification of saturated fats with unsaturated oils	TAGs containing SCFAs TAGs with intermediate properties of substrates
Monoacylglycerols (MAGs)	• Emulsifiers • Emulsifiers with essential fatty acids	Ethanolysis of various TAGs using *sn*-1,3-specific lipases	2-MAG 2-MAG with essential fatty acids
Diacylglycerols (DAGs)	• Emulsifiers DAG oils • Hypotriglyceridemic effects • Anti-obesity effects	Glycerolysis with various FFAs using sn-1,3-specific lipases	*sn*-1,3 DAG
Structured Phospholipids (PLs)	• Emulsifiers	Hydrolysis of *sn*-2 acyl group using PLA_2 phospholipase	PLs with 1 acyl group attached (lysophospholipids)
	• Phospholipids enriched with n-3 and MCFAs • More bioavailable carrier of fatty acids	Acidolysis/transesterification of various FFAs/ ethyl esters with lipases or PLA_1 and PLA_2 phospholipases	PLs enriched with various fatty acids
	• Enzymatic degumming	Hydrolyzing acyl groups on PLs with PLA_1 or PLA_2	Hydratable PLs

[a] Where abbreviations are as described; TAG, triacylglycerol; FFA, free fatty acids; M, medium chain fatty acid; L, long chain fatty acid; ARA, arachidonic acid; DHA, docosahexaenoic acid; P, palmitic acid; O, oleic acid; St, stearic acid; SCFA, short chain fatty acid; LCFA, long chain fatty acid; MCFA, medium chain fatty acid; PLA_1, phospholipase A_1; PLA_2, phospholipase A_2.

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